PB-220 202

MONITORING INSTRUMENTATION FOR THE MEASUREMENT OF SULFUR DIOXIDE IN STATIONARY SOURCE EMISSIONS

TRW Systems Group

Prepared for:

Environmental Protection Agency

February 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

EPA R2-73-163
February 1973

ENVIRONMENTAL PROTECTION TECHNOLOGY

PB 220 202

Monitoring Instrumentation For The Measurement Of Sulfur Dioxide In Stationary Source Emissions

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Springfield VA 22151

Office Of Research And Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-R2-73-163	2.	3. Recipient's Accession No. PB-220 202
4. Title and Subtitle Monitoring Instrumentation for the Measurement of Sulfur Dioxide in Stationary Source Emissions			5. Report Date February 1973 6.
7. Author(s) Fredric C. Jaye, EPA			8. Performing Organization Rept. No.
9. Performing Organization Name and Address TRW Systems Group One Space Park Redondo Beach, California 90258			10. Project/Task/Work Unit No. 17205 11. Contract/Grant No. EHSD-71-23
12. Sponsoring Organization Name and Address Environmental Protection Agency Office of Research and Monitoring Washington, D. C.			13. Type of Report & Period Covered Final Sept.1970-Sept.1971 14.
15. Supplementary Notes Prepared by EPA Project Officer			

16. Abstracts

This report covers work done by TRW Systmes group to assess the state of the art in automatic SO_2 monitoring systems for fossil fuel fired combustion units. The results indicate that adequate monitoring equipment is available to meet EPA New Stationary Source Performance Standards monitoring requirements as long as the units are dealt with as total systems-(i.e. probe, sample conditioning, and analyzer as an integral unit.) Equipment selections were made on an arbitrary basis from that equipment available in December 1970 and was not intended to be monitor vs. monitor comparative or all inclusive in any manner. No approval, certification, recommendation, or acceptance is made or implied other than for the very specific purposes clearly stated in the report.

17. Key Words and Document Analysis. 17a. Descriptors

Key Words:
monitoring instrumentation, air pollution measurements systems, stack monitoring, source monitoring.

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
release unlimited	UNCLASSIFIED	129
	20. Security Class (This Page) UNCLASSIFIED	22. Price

FORM NTIS-35 (REV. 3-72)
USCOMM-DC 14952-P72

EPA-R2-73-163

Monitoring Instrumentation For The Measurement Of Sulfur Dioxide In Stationary Source Emissions

By

Fredric C. Jaye
Based on Information Obtained from Contract with
TRW Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. EHSD 71-23
Program Element No. 1A1010

Project Officer: Fredric C. Jaye
Chemistry and Physics Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared For
Office of Research and Monitoring
Environmental Protection Agency
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February 1973

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Foreword

In March of 1970, the Division of Process Control Engineering issued a Request for Proposal to provide an "Evaluation of sulfur dioxide monitoring equipment for stationary sources." The purpose of this program was to provide the data and evaluation of performance under actual industrial application which would permit the intelligent selection of monitoring equipment for a specific application.

On 2 September 1970, TRW Systems Group, Redondo Beach, California initiated work under contract EHSD-71-23 with Dr. Robert M. Statnick, Division of Process Control Engineering, as the EPA project officer. With the reorganization of EPA and the subsequent transfer of pollutant measurement development work to the Division of Chemistry and Physics, National Environmental Research Center, Dr. Fredric C. Jaye replaced Dr. Statnick as the EPA project officer in March 1971.

The contract was terminated on 29 September 1971 for the convenience of the government at the end of the field test phase (Task G).

The data analysis was performed by members of the Stationary Sources Emissions Measurements Methods Section of the Division of Chemistry and Physics.

This final report was prepared by members of that section and with the exception of task H and conclusions is largely derived from the monthly progress reports submitted by TRW.

ACKNOWLEDGEMENTS

A considerable effort was put forth by the project personnel to prepare the preliminary specifications and instrument evaluations in the attachments. This section is to acknowledge the individuals responsible for the first draft specifications.

APPENDIX	TITLE	TRW PROJECT PERSONNEL
B-1	Proposed General Operating Specifications for SO_2 Stack Gas Monitoring System	J. Eynon
B-2	Specific Design, Manufacture and Use Specifications	G. I. Gruber & A. A. Lee
D-1	NDIR Instrumentation for Stack Gas Monitoring	E. Tagliaferri
D-2	Electrochemical Instruments for Monitoring SO_2 in Stack Gases	R. R. Sayano & E. T. Seo

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INTRODUCTION

The objective of this program was to evaluate and rank commercially available sulfur dioxide monitoring instrumentation for fixed combustor sources. To accomplish this objective the project was organized into eight tasks which provided for a logical review of available instruments and specifications in terms of established use-criteria, selection and procurement of the most promising instruments and finally a field test program where the instruments were installed and operated continuously under real, fixed combustor stack conditions. Instrument performance was rated on criteria including accuracy, specificity, reliability, maintainability, ruggedness and other selected performance criteria. The ranking of instruments was necessarily dependent on the order of importance the potential user places on the established performance criteria.

Task titles with brief content descriptions were as follows:

Task A - Data Search and Acquisition - Obtain from manufacturers and other sources available information on commercial SO_2 continuous monitors suitable for monitoring stationary sources.

Task B - Formulation of Instrumentation Specifications - Formulate specifications that continuous sulfur dioxide analyzers must meet for R/D studies and stationary power plants.

Task C - Acquisition of Data on Existing Installations - Obtain field evaluation data to aid in assessment of instrument applicability, minimize costs of field testing, obtain pertinent data on sampling and handling techniques and desirable instrumentation modifications.

Task D - Evaluation of All Instruments - Compare vendor specifications and user reported performance data with the specifications developed in Task B and rank instruments.

Task E - Design of Test Procedure and Experimental Plan - Generate detailed: 1) design plans, 2) instrument procedures, 3) operation plan, 4) control analysis, and 5) document formats.

Task F - Procure and Install SO_2 Monitoring Equipment - Procure the selected SO_2 monitoring equipment, sampling manifolds, and install them.

Task G - Field Test Program - Conduct the field test program for six months.

Task H - Data Evaluations and Conclusions - Provide a detailed evaluation of the applicability and limitations of the specific instrumentation tested.

At the project kickoff meeting held on 7 October 1970 at TRW's Redondo Beach Facility and attended by Jim Dorsey and Robert Statnick of EPA along with Arnie Grunt, Paul Testerman, Pete White, Al Lee, Fred Harpt, Jim Eymon, Jerry Gruber, Don Wolpert, and Norm Garner of TRW, Project Objectives, tasks and technical approach were reviewed and restated.

During this meeting the following project philosophy and points of emphasis were discussed.

> If at all practical the field testing of instruments will be accomplished on a pulverized, coal-fired boiler of at least 50 megawatts or larger generation capacity. The rationale for the decision is that the majority of power generating plants do burn coal which may give rise to unique and significant interferences from the metals and other coal constituents.

Fuel must, in general, be consistent in type and composition, as would be the case from a single mining area.

The SO_2 concentration of interest will range from 200 to 700 ppm.

Where practical, the instrument manufacturers sampling and pretreatment methods will be utilized.

TASK A

Data Search and Acquisition

Persuant to Bureau of the Budget survey clearance No. 158-S71010, letters of inquiry were sent to all identified and potential manufacturers and representatives of SO_2 monitoring instruments (over 220). From this data search, a list of 18 companies claiming to manufacture or sell SO_2 monitoring instruments suitable for stationary source monitoring was compiled. These companies are listed in Table A-1. Table A-2 contains a number of companies who indicated that they were in the development or marketing survey stage as of 1 January 1971.

Of these companies several units have since become available in the commercial market. These companies are:

Environmental Data Corporation

Melloy Laboratories

Theta Sensors

A number of gas chromatography equipment manufacturers had indicated that while they do not market a G.C. system specifically designed and produced for SO_2 monitoring, that process G.C. systems could be produced to accomplish the task. Table A-3 shows these manufacturers and some brief comments furnished by them.

As a result of several months of survey effort the following sulfur dioxide monitoring equipment for stationary source use was considered as commercially available as of February 1, 1971. See Table A-4.

At the conclusion of this identification task, sufficient information and commercially available monitoring equipment were available to begin Task B, Formulation of Instrument Specifications.

TABLE A-1

MANUFACTURERS OR VENDORS OF SO_2 STACK GAS MONITORS

AERO-VAC CORPORATION
P. O. Box 447
Troy, N. Y. 12181
(518) 274-5850

ANALYTICAL INSTRUMENT DEVELOPMENT
250 S. Franklin St.
West Chester, Pa. 19380
(215) 692-4575

ATLAS ELECTRIC DEVICES CO.
4114 No. Ravenswood Ave.
Chicago, Ill. 60613
(312) 327-4520

BARTON, ITT
580 Monterey Pass Rd.
Monterey Park, Calif. 91754
(213) 283-6501

BECKMAN INSTRUMENTS, INC.
2500 Harbor Blvd.
Fullerton, Calif. 92634
(714) 871-4848

BENDIX CORP.,
PROCESS INSTRUMENTS DIV.
P. O. Drawer 477
Ronceverte, W. Va. 24970

CALIBRATED INSTRUMENTS, INC.
17 W. 60th St.
New York, N. Y. 10023
(212) 245-5590

CANADIAN RESEARCH INSTITUTE
85 Curlew Dr.
Don Mills, Ontario, Canada
(416) 445-6363

E. I. DU PONT COMPANY
1007 Market St.
Wilmington, Del. 19898
(212) 649-9600

DYNASCIENCES CORPORATION
9601 Canoga Avenue
Chatsworth, Calif. 91311
(213) 341-0800

ENVIROMETRICS INC.
13311 Beach Avenue
Marina Del Rey, Calif. 90291
(213) 391-8268

INTERTECH CORPORATION
262 Alexander St.
Princeton, N. J. 08540
(609) 452-8600

KIMOTO ELECTRIC CORP. LTD.
42 Funahashi-Cho
Tennoji-Ku
Osaka, Japan

MINE SAFETY APPLIANCE CO.
201 N. Braddock Ave.
Pittsburgh, Pa. 15208
(412) 241-5900

OLSON HORIBA
1021 Duryea Ave.
Irvine Industrial Complex
Santa Ana, Calif. 92705
(714) 540-7874

SCIENTIFIC INDUSTRIES, INC.
150 Herricks Rd.
Mineola, N. Y. 11501
(516) 746-5200

SCOTT AVIATION/DAVIS INSTRUMENTS
Charlottesville, Va.
(703) 973-5366

VAN WATERS & ROGERS/WILL SCIENTIFIC
1363 S. Bonnie Beach Place
Los Angeles, Calif. 90054
(213) 269-9311

TABLE A-2

SULFUR DIOXIDE MONITORS CURRENTLY UNDER DEVELOPMENT

AS OF 1 JANUARY 1971

Manufacturer	Comments
Anacon Inc. 62 Union St. Ashland, Mass.	
Bacharach Instrument Co. 625 Alpha Drive Pittsburgh, Pa.	Currently have instrument in development.
Burhans-Sharpe P. O. Box 3906 Seattle, Washington	Purchased rights for manufacture and sale of U.V. in-stream analyzer from Weyerhaeuser Co.
Combustion Equipment Association 61 Taylor Reed Drive Glenbrook, Connecticut	Hold the rights to manufacture and sell Barringer SO_2 in-stack monitor.
*Environmental Data Corporation 608 Fig Avenue Monrovia, Calif.	Has one NO in-stack analyzer on a power plant.
Environmental Instruments Co. 1346 Willow Road Menlo Park, Calif.	Developing a mass spectrometer analyzer system for air and stack gases.
General Monitors, Inc. 3019 Enterprise St. Costa Mesa, Calif.	Developing solid state SO_2 and NO_x monitors which are based upon changes in the chemical activity of solid state sensors.
Gow-Mac Instrument Co. 100 Kings Road Madison, N. J.	
Kimoto Electric Corp., Ltd. 42 Funahashi-Cho Tennoji-Ku Osaka, Japan	Manufacture U.V., coulometric and conductometric instruments.
*Melloy Labs 6631 Iron Place Springfield, Virginia	Flame photometric total sulfur analyzer.

TABLE A-2 (Continued)

Manufacturer	Comments
Monitor Labs, Inc. 10451 Roselle Street San Diego, Calif.	An emission spectrophotometer that measures radiation from heated SO_2 in the I.R. region.
Research & Development Products 1808A Harmon Street Berkeley, Calif.	Developing an SO_2 monitor.
Rockland Instrument Corporation P. O. Box 205 Pearle River, New York	Have a reflectance colorimetric tape system under development.
Scientific Research Instruments 6707 Whitestone Road Baltimore, Maryland	Developing a mass spectrometer monitoring system.
* Theta Sensors 1015 No. Main St. Orange, Calif	Developing a fuel cell type monitor.
2000 Corporation 5899 So. State St. Salt Lake City, Utah	Have a wet chemical analyzer under development.
Wilkens-Anderson Co. 4525 W. Division St. Chicago Ill.	In the early stages of developing a stack gas monitor.
Wilks Scientific Corp. 140 Water St. So. Norwalk, Connecticut	Developing an I.R. in-stack monitor.

*Now commercially available.

TABLE A-3

MANUFACTURERS OF GAS CHROMATOGRAPHIC INSTRUMENTS EXPRESSING INTEREST IN SO_2 STACK MONITORS

Analytical Instrument Development Inc. 250 S. Franklin St. Westchester, Pa. 19380	Produce portable G.C.
Antek Instrument Inc. P. O. Box 7903 Houston, Texas 77007	Developing G.C. No field test. No users.
Applied Automation Inc. 3838 S.E. State St. Bartlesville, Oklahoma 74003	Developing G.C. No field test. No users.
Beckman Instrument Inc. 2500 Harbor Blvd. Fullerton, Calif. 92634	Process chromatograph used on stacks with customer developed technology.
Chemical Data Systems Inc. Oxford, Pa.	Developing G.C. No field test. No users.
Process Analyzer Inc. 6400 W. Freeway, Suite 400 Houston, Texas 77036	Process chromatograph. No field test.
Tracor, Inc. 6500 Tracor Lane Austin, Texas 78721	Process chromatograph. No field test. No users.
Unico Environmental Instruments P. O. Box 590 Fall River, Mass. 02722	Developing G.C. No field test. No users.
Carle Instruments, Inc. 1141 E. Ash Ave. Fullerton, Calif.	Column 10% didecyl phthalate on chromosorb T. 40-60 mesh. Can determine CO_2, SO_2, and H_2O.

TABLE A-4

INSTRUMENTS COMMERCIALLY AVAILABLE

AS OF 1 FEBRUARY 1971

	Comments
UV-Vis	
DuPont 460[a]	Only currently available UV-Vis analyzer suitable for stack gas monitoring. Good reports have been received from users.
NDIR	
Intertech[a]	Good reports have been received on this instrument. Appears to be of good design and construction.
Bendix[a]	No users located to date. Some new concepts, etc. were utilized in design and construction. Appears to be an excellent instrument.
Beckman[a]	Most user information satisfactory.
M.S.A.	No user information obtained to date. In general M.S.A. has a reputation for good construction.
Horiba, Ltd.	Instrument to be marketed in the U.S. in the near future. Distributor will send information as soon as received from Japan.
Electroanalytical	
Dynasciences[a] SS330/CS1000	Fuel cell type.
Enviro Metrics S-64[a]	Same as above.
Calibrated Instruments[a]	Conductometric type.
MSK-SO_2E_1	
Scientific Industries Model 70	Conductometric type.
ITT Barton Model 400	Coulometric type.

TABLE A-4 (Continued)

Other	Comments
Aero-Vac Model 170-200	Mass spectrometer.
Environmental Data[b]	In stream spectrometric type.

[a]Instruments recommended for inclusion in the field evaluation.

[b]Based on our search and verbal contacts with the vendor we were unable to ascertain that an SO_2 in-stack monitor had been produced.

TASK B

Formulation of Instrument Specifications

Prior to any laboratory or field testing of SO_2 monitoring equipment, it was necessary to establish those criteria which are considered important in the evaluation of the usability of such equipment and to propose target goals for each area. As of the time of initiation of this program, the only widespread utilization of SO_2 monitoring equipment was in the Federal Republic of Germany and some use of ambient air monitors here in the United States. Therefore, we were required to formulate these general requirements on the basis of limited information and rely heavily on engineering judgment.

Table B-1 is a brief summary of the external environmental conditions based on a cross section of United States weather. This information was taken from "Climate Atlas of the United States" (June 1968), U. S. Department of Commerce. The table clearly indicates that all instrumentation will have to be protected and that the sampling system must be protected, insulated and have sufficient heating power to keep the sample in gaseous form.

General Instrument Specifications -

The following instrument generalizations, exclusive of sample probe and preconditioner were presented for consideration:

Selectivity-measure SO_2 content and relate the content measured to the original stream SO_2 content--define interferences and required correction or sample pretreatment.

Routine operation - unmaintained for extended periods of time (up to 1 week excluding recording device) with specified stability, accuracy and reproducibility (see below).

Calibration - capable of calibration and standardization by a power plant instrument technician, without special training or unique equipment.

Maintenance/Repair - capable of being maintained by a qualified power plant instrument technician or be subject to readily available contract maintenance service. Parts availability must be on a maximum 24-hour basis from nearest supply point, for any and all parts required for repair. Shelf life on parts stock in power plant instrument warehouse shall be minimum of two years. Special charts and inks are considered as "parts." Mean time to repair the unit should have a goal of 2 hours while maximum time to repair shall have a goal of 8 hours.

Reliability - long term reliability of SO_2 monitor system must be compatible with the monitoring needs of the power plant, i.e., instrument must operate most of the year with minimum repair/replacement; normal annual preventive maintenance/refurbishment shall be accomplished during the annual down time of the power unit.

Output signal - instrument outputs shall be linear analog or equivalent signals capable of immediate interpretation in SO_2 conc. units (vol.).

Recording - linear analog or equivalent in SO_2 vol. conc. units by fractional hour, with minimum 24 hour chart capability ±1.5% of indicated instantaneous value. Accessibility for chart replacement/notation via hinged instrument case required.

Operating Specifications

Operating specifications for specific instruments may have to be developed for each general type depending on principle. Discussions with power plant engineers and TRW project personnel indicated, however, that certain tentative common operating specifications may be delineated at this time. For example, operating accuracy is derived from the combination of absolute accuracy, reproducibility, drift, interference and many other factors, and must be within

certain known limits if the final measurement is going to be meaningful. The following preliminary instrument operating specifications were developed to meet the need for a recorded SO_2 concentration value that relates meaningfully to the effluent SO_2 concentration.

Accuracy - ±2% of span as measured against standard referee chemical test procedure.

Reproducibility - 1.0% of span

Zero Drift - 24 hr ±0.8% of span
7 day ±2.2% of span

Span Drift - 24 hr ±0.8% of span or ±0.002% of SO_2 (which ever is larger)

7 day ±2.2% of span or ±0.006% of SO_2 (which ever is larger)

Sensitivity - sufficient to detect a 5 ppm change in SO_2 concentration when the instrument is operating in the 200-700 ppm range(s).

Temperature, Voltage, and Pressure Variations - sufficient stability to meet above specifications when reasonably protected from adverse power plant environment. (Nominal Operating Conditions--
Temperature $70^{\circ} \pm 20^{\circ}$ F,
Relative Humidity 0-90%,
Voltage at Stated Value ± 20%).

Utilizing these preliminary specifications, the intended use environment, the manufacturers' specifications and generally accepted state-of-the-art, the TRW project team generated two more detailed specifications. Appendix B-1 provides a set of general operating specifications. Appendix B-2 provides a set of guidelines with requirements for design, fabrication, performance and testing that would be required in a controlling document for manufacture.

TABLE B-1

U. S. Climatic Conditions by Region

Location: National Area and Cities	Mean Annual Days 90°F or Greater	Mean Annual Days 32°F or Less	Extreme Daily Temperature °F and R.H. January High	January Low	January R.H.	July High	July Low	July R.H.%	Average Annual Total Precipitation, Inches (as rain)	Average Annual Total Precipitation, Inches Snow	Fastest Wind Direction	Fastest Wind Velocity M.P.H.
West Coast	0-5	10-20								0-12		
Seattle, Wash.			67	3	90	100	46	90	100	<12	S	65
Los Angeles, Calif.			90	28	65	109	49	70	17	0	N	49
(Inland areas incl. mountain areas)	20-120	20-210								12-400		
Southwest	2-90	10-210								0-60		
Las Vegas, Nevada			76	8	40	117	56	20	5	<6		
Flagstaff, Arizona			65	-30	55	93	32	40	14	24	SW	72
El Paso, Texas			77	-8	60	109	56	50	12	22	NW	70
Northwest	2-20	90-240								24-200		
Boise, Idaho			63	-17	80	111	40	40	25	24	W	61
Mountain States	0-5	150-240								36-400		
Denver, Colo.			76	-20	60	104	42	50	16	60	W	65
Western Plains	20-90	60-180								1-36	W	72
Bismarck, N. Dakota			60	-45	70-80	114	32	65	18	12-24	N	100
Wichita, Kansas			74	-15	60-70	117	53	55	20-25	4	WSW	67
Midland, Texas			83	-8	60	107	71	50	22			
Middle States (Midwest to Gulf Areas)	5-90	10-180								0-100		
Minneapolis, Minn.			58	-34	70-80	108	44	70	28	36-60	W	92
Chicago, Illinois			67	-20	70-80	105	49	70	36	36-60	NE	87
Pittsburgh, Pa.			75	-18	70-80	103	42	70	40	36	NW	73
St. Louis, Missouri			77	-22	70-80	115	51	65	34	12-24	SW	82
New Orleans, La.			83	13	80	102	66	80	62	0	SE	98
Appalachian Area	2-20	120-150	75	-15	70	103	45	80	45	12-100	-	-
New England	2-10	10-180								24-100		
Caribou, Maine			51	-32	80	95	40	70	40	100	NW	76
Boston, Mass.			72	-13	80	104	50	80	43	36-60	S	87
Eastern Seaboard	5-60	0-90								0-60		
New York, N.Y.			72	-6	70	106	57	80	45	36	SE	113
Washington, D.C.			79	-14	70-80	106	57	80	45	12-24	SE	78
Charleston, S.C.			82	10	80	104	61	90	46	<1	-	76
Miami, Florida			83	31	80	95	65	80	60	0	E	132

APPENDIX B-1

PROPOSED GENERAL OPERATING SPECIFICATIONS FOR SO_2 STACK GAS MONITORING

by J. Eynon

1. Scope

This document is intended to delineate the desired general operating specifications for SO_2 stack gas monitoring instrumentation as a guide for the evaluation and selection of such equipment. The equipment is for continuous monitoring of SO_2 in the effluent gases from the combustion process in electric utility power plants using fossil fuels. It is to be comprised of a sampling system, including any necessary sample conditioning equipment, and a measuring system including an analyzer and recorder.

2. Measuring System

Proposed operating specifications for the measuring system are as follows:

2.1 Range

0 to 3000 ppm SO_2 in one step is required; provision for selecting a shorter span, such as 0 to 1000 ppm SO_2 is a desirable option.

2.2 Sensitivity

Sufficient to detect a change of 10 ppm in SO_2 concentration at each of the span of concentrations covered by the analyzer.

2.3 Readability

Scale of the readout device shall be direct reading in SO_2 concentration and have sufficient resolution to permit concentration to be read within 10 ppm.

2.4 Limit of Error

After the span of the measuring instrument has been set under fixed conditions of temperature, pressure, and line voltage using a zero gas and a span gas of known SO_2 concentration, the

calibration of the scale is to be checked using four gases of known SO_2 concentrations corresponding to approximately 25%, 50%, 75%, and 100% of full scale. The readings should agree with these known SO_2 concentrations with a limit of error of ±1%. Over a period of 7 days of unadjusted operation, the readings of the analyzer as compared with values obtained by the standard referee chemical test procedure, shall have a maximum error of ±5%.

2.5 Zero Drift

Definition: The change with time in instrument output at a constant concentration of 0.00 ppm SO_2 over a given period of unadjusted continuous operation of the analyzer.

Specification:

24 hour period:	± 1% of span
7 day period:	± 2% of span

2.6 Span Drift

Definition: The change with time in instrument output at a constant concentration of SO_2 over a given period, exclusive of zero drift.

Specification:

24 hour period:	± 1% of span
7 day period:	± 2% of span

2.7 Noise

For a constant value of SO_2 concentration in the sample gas, short term fluctuations in the recorded readings shall not exceed the equivalent of 0.5% of full scale during a period of 10 minutes.

2.8 Repeatability

Definition: Differences in successive readings obtained for a gas sample containing a constant amount of SO_2 when it is applied to analyzer alternately with a gas sample containing no SO_2.

Specification: ±.5% of span.

2.9 Selectivity

Analyzer must be selective for SO_2 and discriminate against variations of other constituents in the background gas from fossil fuel combustion. These constituents typically include, but are not limited to the following:

Constituent	Concentration Range
SO_2	0 to 3000 ppm
CO	0 to 50 ppm
CO_2	12 to 18%
H_2O	4 to 14%
NO_x (as NO_2)	50 to 800 ppm
SO_3	0 to 100 ppm
O_2	1 to 5%
N_2	Balance

Response of analyzer to such variations must not be greater than 1% of span or 10 ppm SO_2.

2.10 Ambient Pressure Influence

Variations in atmospheric pressure of ± 1 inch of mercury from the value at which the SO_2 monitor is calibrated shall not cause more than ±0.3% variation in the reading.

2.11 Ambient Temperature Range

The equipment, exclusive of the sampling probe located in the stack, shall be capable of operating over an ambient temperature range from 0°C to 50°C (32° to 122°F).

2.12 Ambient Temperature Influence

Variations in ambient temperature shall not cause variations in readings of SO_2 monitor in excess of ±0.1% of reading per degree Centigrade, assuming maximum rate of temperature change is 10°C/hour (18°F/hour).

2.13 Power Requirement

The equipment shall operate on 120 volts ± 20%, AC, 50 to 60 Hz.

2.14 Line Voltage Influence

Variations in line voltage from a nominal voltage of 120 volts shall not cause variations in reading of the SO_2 Monitor in excess of 0.01% per volt.

2.15 Lag Time

Definition: The time interval from a step change in SO_2 input concentration at the instrument inlet to a readable change in recorded output.

Specification: Not more than 10 seconds.

2.16 Response Time

Definition: The time interval from a step change in SO_2 input concentration at the instrument inlet to a recording of 90% of the ultimate recorded output.

Specification: Not more than 1 minute.

2.17 Local Indication

An indicator, calibrated to read directly in SO_2 concentration, shall be provided in the monitor location.

2.18 Remote Indication

A DC output signal shall be provided to operate a potentiometric type recording instrument. Minimum output signal level should be 0 to 10 millivolts, corresponding to the full span of SO_2 concentration measured by the analyzer.

2.19 Sample Temperature

The monitor should be capable of operating with the sample cell at a temperature in excess of the expected maximum dew point of the sample (See Section 3).

2.20 Construction

2.20.1 The construction and finish of the equipment are to be suitable for the industrial environment of an electric power plant.

2.20.2 Components of the equipment which will contact the sample gas are to be constructed of materials which are inert to the constituents of the sample gas, i.e., which do not alter the SO_2 content of the sample and are corrosion resistant.

2.20.3 Modular construction insofar as possible is preferred so that faults may be quickly located and corrected by replacement of the faulty module.

2.20.4 Electronic circuits preferable shall be of modern solid-state design with modular printed circuit boards. All components shall be conservatively rated; and fabrication and workmanship shall conform to good commercial practice.

2.20.5 All necessary equipment for adjustment and control of sample flow rate and reagent supply system (if reagents are required) are to be furnished with the analyzer.

2.20.6 Provision shall be made so that zero and span test gases may be connected to analyzer conveniently either by a valving system or by disconnection and reconnection of a simple fitting.

2.21 Mounting

The instrument shall be suitable for either flush (panel) or wall mounting.

3. Sampling System

The sampling system including any necessary sample conditioning equipment shall not alter the SO_2 content of the sample and shall permit operation of the analyzer with sample gases having typical composition and temperature as follows:

SO_2	0 to 3000 ppm
Temperature	200°F to 900°F
Fly-ash content	up to 5 grains per standard cubic foot
CO_2	12 to 18%
CO	0 to 50 ppm
H_2O	4 to 14%
NO_x (as NO)	50 to 800 ppm
SO_3	0 to 100 ppm
O_2	1 to 5%
N_2	Balance
HC	0 to 1500 ppm

APPENDIX B-2

SPECIFIC DESIGN, MANUFACTURE AND USE SPECIFICATIONS

by G. I. Gruber and A. A. Lee

INTRODUCTION

The following document is to serve as criteria for the selection of SO_2 Monitoring Systems for fixed combustion sources and may serve as a guide for the manufacture of such instruments.

1. SCOPE

1.1 Scope

This specification establishes the requirements for the design, fabrication, performance, and testing of a fixed location SO_2 gas concentration, sample measuring and recording instrument system. (SO_2 fixed combustor stack gas monitor) The system is to be used to continuously determine quantitatively the concentration of SO_2 gas in exit gas from stationary power plants using fossil fuels.

2. APPLICABLE DOCUMENTS

2.1 Government Documents

The following documents are intended as a guide to good practice in design, fabrication, testing and manufacturers literature preparation for the purposes of this specification.

SPECIFICATIONS

Military

MIL-C-5015	Connectors, Electrical AN Type
MIL-S-6872	Soldering Process, General Specification for

STANDARDS

Federal

Fed Std No. 596 Colors

Military

MIL-STD-15	Electrical and Electronic Symbols
MIL-STD-16	Electrical and Electronic Reference Designation
MIL-STD-454	STD General Requirements for Electronic Equipment
MIL-STD-202	Test Methods for Electronic and Electronic Components Parts
MIL-STD-1472	Human Engineering Design Criteria for Military Systems, Equipment and Facilities
MS33586	Metals, Definition of Dissimilar

Other

(a) Emissions From Coal Fired Power Plants: A comprehensive summary U. S. Department of Health, Education, and Welfare, NAPCA, Cuffee and Gerstle 1967

(b) Performance characteristics of Instrumental Methods for Monitoring Sulfur Dioxide, JAPCA Volume 19, No. 8, August 1969, Rodes, Palmer et. al U.S. Department of Health, Education, and Welfare Public Health Service.

3. REQUIREMENTS

3.1 Qualification

The unit described by this specification shall be a product which has passed all the examinations and tests specified in the following.

3.2 Materials

The unit to be constructed of materials of the corrosion-resistant type or suitably treated to resist corrosion caused by NO_2, SO_2, SO_3, or H_2SO_4, salt spray, or atmospheric conditions likely to be met in storage or normal service.

3.2.1 Dissimilar Metals

Unless suitably protected against electrolytic corrosion, dissimilar metals shall not be used in intimate contact with each other. Dissimilar metals are defined in Standard MS33586.

3.2.2 Design and Construction

The monitor system may be a combination pneumatic-electromechanical/electrochemical/optical-electronic instrument. It shall consist of the following major systems:

a) Sampling probe, b) sampling lines and valves, c) sample gas pump, d) analyzer, e) recorder, f) calibration and back purge system as required by the sensing technique employed.

3.2.2.1 Derating of Electronic Parts

All electronic parts should be derated as follows:

(a) Capacitors: Minus 25 percent of working voltage.

(b) Resistors: Minus 25 percent of working power dissipation plus an additional minus 25 percent for precision resistors (tolerances less than plus or minus 1 percent).

(c) Transistors: Minus 25 percent of working power or current.

(d) Transformers and Inductors: Minus 10 percent of voltage and 10 percent of current ratings.

(e) Relay and Switch Contracts: Minus 10 percent of a maximum current - allow additional derating for elevation above sea level.

(f) Diodes and Rectifiers: Minus 25 percent of current or voltage, or minus 25 percent of power, whichever is greater. In all cases use lowest possible operating temperature.

Derated operating values of electronic parts are not to be exceeded whenever the equipment is subjected to the service conditions specified herein. As a guide, even under the maximum load conditions, the recommended safe load rating of the part is not to be exceeded.

3.2.2.2 Power

The system should be designed to operate from a 120V± 15 percent 60±1 H, AC power source.

3.2.2.3 Indicators

The instrument shall be equipped with a readout meter. The meter shall be installed on the face of the detector case in such a position that the operator's line of sight to the meter will not be obstructed during normal use including calibration. The meter scale shall have at least 100 divisions (preferably 200) between 0 and 1000 ppm. (Scale markings shall be 0 to 1000 ppm.)

3.2.2.4 Analyzer Integration

The monitor shall be integrated into a unit that will provide for simultaneous reading of the meter and the recorder.

3.2.2.4.1 SO_2 Monitor

The analyzer shall be used to detect SO_2 gas from power plant stacks. The analyzer shall be calibrated with the use of fixed concentration sources of SO_2 gas and shall cover its range in a minimum of 4 calibration points.

Range	App SO_2 Concentration
Low Range	0-200 ppm
STD Range	450 ppm
High Range	700 ppm
Span	1000 ppm

3.2.2.5 Interferences

The SO_2 analyzer should not indicate a total error reading greater than 5 ppm or 1% of span whichever is greater for all constituents other than SO_2 of the stack gas. The composition normally found in a stack gas include but are not limited to the following gaseous substances:

	App. Range
NO	100-700 ppm
NO_2	0-100 ppm
CO	0-50 ppm
CO_2	12-18%
H_2O	4-14%
O_2	1-16%
SO_2	200-1000 ppm
SO_3	0-100 ppm
N_2	

Other characteristic stack gas substances are shown in tables 1, 5, and 7 of Reference (a) (under 2.0).

3.2.2.6 Calibration of Monitor or Analyzer

The unit shall be designed so that calibration and preventive maintenance may be performed on it with a minimum disassembly, other than removal of minor fittings.

3.2.2.7 Calibration Adjustments

Calibration adjustments should be of the locking screw type, or where adjustments are mounted internally on sub-chassis, circuit boards, etc., adjustments may be of the trimmer type employing a worm drive screw mechanism capable of retaining its setting when subjected to shock and vibration. External adjustments which must be operated by the user should have control knobs and shall be equipped with hand operated locking devices. Such controls should be conveniently located.

3.2.2.8 Soldering

Soldering shall be in accordance with good practice. (Ref. MIL-S-6872)

3.2.2.9 Connectors

All external electrical connectors shall be of good quality and of the lock-on type. (Ref. MIL-C-5015)

3.2.2.10 Wire and Wire Harness

Wire used to accomplish electrical interconnection between components or parts within the systems may be routed individually or as a part of wire harness. Such wire shall meet the requirements of good commercial practice. All wires shall meet Underwriters Laboratory requirements for insulation.

3.2.2.11 Jumpers

Jumpers not exceeding 4 inches in length may be fabricated from uninsulated solid copper wire having a cross sectional area not less than the cross sectional area specified for AWO-24 wire. Where required to provide adequate dielectric strength, such jumpers may be covered with an insulating sleeve.

3.2.2.12 Self-tapping Screws

Thread-cutting screws shall not be used in the design; however, self-tapping screws may be used to mount identification plates.

3.2.2.13 Calibration

The monitor system should be capable of automatic calibration or the necessary equipment for calibration should be supplied with the system. In the case of an automatically calibrating system the use of automatic feature for the long term stability checks (24 hour and 7 day) etc. will be allowable.

3.2.2.14 Sampling Flow Rate

The unit shall be capable of providing a sampling flow rate of 4 liters (NTP) per minute minimum, or twice that required for the specific instrument, which ever is greater.

3.3 Shelf Life

The instrument and stored spare parts shall have the capability of a shelf storage life of not less than 2 years. To place the stored detector in use shall require only cell activation and detector calibration.

3.4 Maintenance

The unit shall be capable of operation for 1 month on a 24 hour per day basis without any maintenance and with weekly unit calibration. Replenishment of normal operating supplies is not considered maintenance. The unit shall be designed and constructed to permit maximum accessibility to parts requiring maintenance or replacement with a minimum use of special tools. It shall be capable of being maintained, repaired, or replaced with a minimum use of special tools. The unit shall insofar as possible be of modular construction, with each module capable of "off-the-shelf" replacement, and shall be capable of trouble diagnosis to the module level with vendor supplied maintenance equipment.

3.5 Human Engineering

The analyzer and arrangement of components therein shall conform to the requirements of good human engineering practice. (Ref. MIL-STD-1472)

3.6 Performance

The unit shall have the following performance characteristics:

3.6.1 System Performance

The total system performance, from probe inlet through the recorder system should be such that the instrument readout versus actual system SO_2 input should not vary more than 3% during any 24 hour period or more than 5% during a seven day period.

3.6.2 Monitor

The monitor shall be capable of reliably detecting SO_2 with a minimum sensitivity of 5 ppm by volume. They shall cover the range of 0-1000 ppm in 3 steps. (Other steps optional) Readings shall have a maximum error of less than 5 percent or 5 ppm, whichever is greater for a period of 7 days of unadjusted operation. Linearity shall be defined by "best fit" straight line starting at zero ppm. No reading shall deviate from this line more than ±5 percent of the readings or 5 ppm, whichever is greater. Instruments that do not

have a linear response must be provided with a direct method of converting response to ppm.

3.6.3 Stability

Span stability shall be within ± 0.8% of Span for 24 hours and ± 2% of Span for 7 days of unadjusted operation.

3.6.4 Response and Sensitivity

The monitor shall respond to a 5 ppm change in SO_2 concentration range of 200-700 ppm. Response, is defined as the time for the indicated valve of SO_2 to reach 90% of the true value when switching from zero gas to 75% span gas at the instrument inlet. The time shall not exceed 90 to 120 seconds. Maximum time for recovery (return to 7.5% of span when zero gas is introduced) shall be less than 90 to 120 seconds.

3.6.5 Inlet and Sample Handling System

The monitor system should be offered with a probe and sample handling system made of material inert to H_2SO_4 etc. which is capable of: a) having the probe operate within the stack environment and b) sample transfer and conditioning outside the stack atmosphere so as to not influence the SO_2 concentration of the sampled stack gases.

3.7 Environmental Conditions

The unit shall be capable of withstanding the environmental conditions indicated in Table 1. The inclusion of internal heaters is permitted. In addition, the unit shall be capable of satisfactory operation in an environment of 120 degrees F (50°C) ambient conditions for an 8 hour period.

3.7.1 Case

The case of the unit shall be constructed and insulated in such a manner that the unit will operate within its specified accuracies for a minimum of 24 hours at a temperature of 32°F (0°C). This may be accomplished by the use of an internal heater, or any other acceptable means.

3.8 Interchangeability and Replaceability

Assemblies, components, and parts having identical part numbers shall, where practicable, meet the requirements for an interchangeable item as defined in 3.8.1. Where interchangeability is not practicable, the requirements for a replacement item defined in 3.8.2 shall apply.

3.8.1 Interchangeable Item

When two or more items possess such functional and physical characteristics as to be equivalent in performance and durability and are capable of being exchanged one for the other without alteration of the items themselves or of adjoining items except for adjustment, and without selection for fit or performance, the items are interchangeable.

3.8.2 Replacement Item

An item which is functionally interchangeable with another item, but which differs physically from the original part in that the installation of the replacement part requires operations such as drilling, reaming, cutting, filing, shimming, etc. in addition to the normal applications and methods of attachment, is known as a replacement item.

3.9 Interference

The unit shall comply, in the 50 kc to 10,000 mc range, with the requirements for susceptibility to rf interference. (Ref: Specification MIL-I-26600.)

3.10 Weight

The weight of each component part of the monitor unit, probe, recorder, etc., shall not exceed 40 pounds.

3.11 Finish

The exterior surfaces of the unit shall meet good standards for finishes of industrial process instrumentation.

3.12 Identification and Marking

The supplier shall attach identification plates to the unit. The plates shall contain the following information: Manufacturer's name, Model number, Part number, serial number.

3.12.1 Electrical and Electronic Reference Designations

Electrical and electronic reference designations shall be in accordance with the commercial abbreviated unit numbering method. (Ref: MIL-STD-16)

3.12.2 Electronic Symbols

Electronic symbols used on drawings in operation and service instructions and on the components of the unit shall be in accordance with good practice. (Ref: MIL-STD-15)

3.13 Workmanship

The monitor shall be constructed and finished in a thoroughly workmanlike manner. Particular attention should be given to the neatness and thoroughness of soldering, wiring, marking of parts and assemblies, welding, brazing, riveting, plating, painting, alignment of parts, tightness of assembly screws and bolts, and freedom of parts from defects, burrs, and sharp edges.

3.14 Operating Manuals

Operation and maintenance manuals shall be supplied with the unit which give detailed instructions for operation, preventive maintenance, calibration trouble shooting, and repair. Detailed schematics of all elements shall be included so that a qualified operator can acquire a knowledge of the system.

Details of the maintenance manuals shall be such that a qualified power plant instrumentation technician shall be capable of trouble shooting using vendor supplied equipment to the repairable module level within 2 hours minimum repair time and a maximum repair time of 8 hours.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for Inspection

Unless otherwise specified in the contract or purchase order, the supplier is responsible normally for the performance of all test requirements.

4.2 Test Procedures

The manufacturer should prepare a test procedure for the implementation of these tests. These procedures should include a description of the methods and devices to be used to establish and control the required test conditions and a detailed step-by-step procedure for conduct of the test.

4.3 Test Samples

The customer may furnish test samples to the supplier, otherwise accurate gas blends should be utilized by the supplier.

4.4 Component Measurement Tolerances

Instruments used to measure test results should be accurate to within 10 percent of the tolerance allowed on the quantity being measured; however, the greatest accuracy required of an instrument under these conditions is no more than 0.5 percent. This requirement does not apply to vapor samples.

4.5 Test Equipment Calibration

The supplier should furnish the customer with evidence of current calibration of test devices and instruments used in the tests specified herein.

4.6 Test Data

The supplier should furnish the customer with a certified copy of the test data.

4.7 Test Conditions

Unless otherwise specified, tests shall be conducted under the following ambient conditions:

(a) Temperature + 59°F to + 95°F

(b) Humidity - 0% to 90% relative humidity

(c) Pressure - 10.0 psia to 15.2 psia

4.8 Testing

Testing should consist of the following examinations and tests as described in 4.10.

(a) Examination of Product (4.10.1)

(b) Functional Test (4.10.2)

(c) Environmental Temperature Test (4.10.3)

(d) Environmental Shock and Vibration Test (4.10.4)

(e) Post Shock and Vibration Functional Test (4.10.5)

4.9 Instrument Test Samples

Samples for the full test series of 4.8 should consist of 2 or more units representative of the production item. Production testing of all items should be determined by the suppliers Quality Control System.

4.10 Test Methods

4.10.1 Examination of Product

The unit should be examined for workmanship, identification, finish, and ease of operation.

4.10.2 Functional Test

While operating at ambient temperature, incremental concentrations of SO_2, to cover the full range of operation of the instrument, shall be introduced at the system inlet and recordings made of the instrument readings. The outputs of the unit shall be as specified in 3.6.

4.10.3 Environmental Temperature Test

4.10.3.1 Preparation for Test

The unit placed in a temperature chamber and stabilized at the required temperature prior to beginning of each step of the test. The stabilization to be determined by the thermocouple method or some suitable alternate methods. Stabilization will be considered established when the readings of the thermocouple are within the specified temperature for three successive readings taken five minutes apart.

4.10.3.2 Test

The unit should first be stabilized within the ambient temperature range of +59°F to +95°F and operation checked. The temperature should then be increased and stabilized at a temperature of 50°C (122°F), then decreased in steps to 0°C (32°F). At each of the temperature increments, the unit should be operated throughout its sensing range for a period of at least 3 hours. The outputs of the unit shall be as specified in 3.6.

4.10.4 Environmental Shock and Vibration Test

The unit shall be tested to values listed in Table 1. (Ref: MIL-STD-202, Method 201.)

4.10.5 Post Shock and Vibration Functional Test

After the shock and vibration tests, a repeat of the functional test described in 4.10.2 should be performed.

5. PREPARATION FOR DELIVERY

5.1 Preservation and Packaging

The unit shall be preserved and packaged in accordance with best commercial practice.

6. NOTES

None

TABLE 1

ENVIRONMENTAL CONDITIONS

	A	B
Environment	Non-Operating (Transportation Storage and Handling) in Packaged Condition, except as noted otherwise	Operating Under Sheltered Environment
Temperature	High: 50°C (122°F) Low: 0°C (32°F)	Same as Column "A"
Humidity (Relative)	0 to 90% rh with conditions such that condensation takes place in form of water or frost	5 - 98% rh intermittant
Vibration	Vibration as encountered by equipment requiring shipment by all modes of common carrier. This vibration is +1.3g from 2 to 27 cps and 3g from 27 to 500 cps	Protected from plant vibrations etc., which could effect operation of the instrument
Shock	Drops on three mutually perpendicular faces on a concrete floor as follows: Cross Weight, lbs. — Height, Inches 50 — 30 100 — 21 150 — 18 200 — 16 600 — 14 3000 or over — 12	None
Salt Fog	50 hours exposure to a 20% salt fog solution	No Requirement
Fungus	As encountered at maximum temperature and humidity	Same as Column "A"
Altitude	Sea Level to 15,000 feet	Sea Level to 6,000 ft.

TASK C

Acquisition of Data on Existing Installations

The original plan for the program envisioned an intensive effort to contact users of SO_2 monitoring equipment and to obtain their comments and operating experience in the field before completing the design of the field test program. This worthwhile idea and plan met with two major snags. First, the required Bureau of the Budget clearance for the survey was not received until the program was nearly completed. Second, there are very few SO_2 monitoring equipment users in the U. S. In retrospect, a total of nine user questionnaires were usable, a number of which would not have required Bureau of the Budget approval at all. Table C-1, essentially, summarizes the responses of these equipment users with the footnote added at the end of the program as hindsight. Most of the users of SO_2 monitoring instruments are located on the East Coast to Midwest regions which in general are the same regions where high sulfur coal is produced. Many power company personnel stated that they were waiting for the regulating legislation defining emission limits and approved means of monitoring before they take action on either removal equipment or monitoring instrumentation.

TABLE C-1

Manufacturer	Number of Returned Questionnaires	User Comments
ITT Barton	1	Instrument was utilized for evaluation only on a pulp and paper mill. Sampling proved to be a major problem; however, instrument performance was excellent.
Beckman	1	Used for measurement of SO_2 in flue gas. Overall instrument performance, etc. was rated as good. Estimated repeatability 2%; estimated accuracy ±10%. Scrubber system should be improved to reduce interferences.
Beckman 315A	1	Used for measurement of SO_2 in flue gas. Overall instrument performance rated as fair to poor. Estimated accuracy 95+ %.
*DuPont Model 400	1	Used for SO_2 measurement in flue gas. Overall performance was rated as excellent for analyzer unit and fair for sampling system. Estimated repeatability ±1%. Estimated accuracy ±1%.
Dynasciences	1	Used for SO_2 measurement in flue gas. Overall rating was poor. Low stability, routine functions, etc. required 2 hrs operator time per day. Estimated repeatability ± 5%. Estimated accuracy ± 10%.
EnviroMetrics S-64S	1	Used for SO_2 measurements in flue gas. Overall rating was fair to good. Estimated repeatability ± 5% at 1000 ppm SO_2.
*Intertech NDIR	1	Used for SO_2 measurements in a power plant. Overall rating was excellent requiring little attention and maintenance. Estimated repeatability ± 2%. Estimated accuracy ± 5%.

TABLE C-1 (Continued)

Beckman Chromatograph 620D	1	Used for SO_2, CO_2, and O_2 in power plant stack gas and cat-ox converter. This unit utilized user developed technology and columns. Overall rating excellent. Average down time 25%. Estimated repeatability ± 1%. Estimated accuracy ± 2-3%.
Leeds and Northrup NDIR	1	SO_2 analysis of $MgSO_3$ waste gases from pump mill. Overall rating poor.

*It should be noted that at the time of this survey (early 1971) these units were the only units on this list which were available as "complete field tested systems."

TASK D

Preliminary Evaluation of Instrumentation

According to the original contract plan, after completing the extensive survey and digesting large amounts of user provided information, the project staff was to evaluate and rank the existing instrumentation according to user information, Task B preliminary specifications, and any other engineering or scientific judgments which could be brought to bear. However, Task C provided very little data, so the staff was forced to make their ranking and evaluation judgments on the basis of very meager and often very subjective data.

Since the rankings and judgments were arrived at in this manner, the following sections were presented in order to fulfill the contract terms and show the effort involved. The remainder of this section on Task D are to be considered as tentative, largely unsubstantiated, and subjective information and comment.

Based on the current information, a preliminary ranking of instruments was performed. To a large extent the rankings, brief comments and problem areas included below, were derived from the information in the attachments.

Ultraviolet - Visible Optical Instruments

At the time the DuPont models 400 and 460 were the only candidate UV-VIS SO_2 stack gas monitors. The others had either withdrawn or had not supplied sufficient information for evaluation.

Non-Dispersive Infrared NDIR (Attachment D-1)

A major potential problem exists with the NDIR instruments, i.e., the stack gas sample must be conditioned to remove H_2O. Such conditioning also removes approximately 5% SO_2. This value can vary with sample conditioner design and operating parameters.

Ranking of instruments for this and other reasons is at best arbitrary without laboratory testing under controlled, comparative conditions. Minimum laboratory testing consists of the following:

a) base line drifts
b) span drifts (at 75% of span)
c) physical inspection of instruments
d) sensitivity to SO_2
e) sensitivity to H_2O

The NDIR instruments were ranked as follows:

1. Bendix Unor
2. Intertech Uras
3. Beckman Model 315A
4. M.S.A. Lira Model 300

The above ranking was based upon design and theoretical operating considerations from limited information. It may be expected that the ranking would change as other assessment criteria, e.g. user information on reliability, accuracy, etc. are applied.

Flame Photometric

This instrument (the only one of its type) is under development by Melloy Laboratories as a potential SO_2 stack gas monitor. A few of the potential application problems include plugging by particulates, the large volume of dilution gas required and potential interference by CO_2. There were no commercially available F.P.D. analyzers. Melloy Laboratories had constructed one "production prototype." The unit was being used for display and was not available for testing on this program. It had been reported verbally that definite interferences occur in the measurement of SO_2 when high concentrations of CO_2 were present. The interference is most likely caused by CO from the dissociation of CO_2 in the flame.

The major problems for this type of detector system include:

a) dilution of 4000 to 1 requirement
b) reported negative interference from CO_2

Mass Spectrometer SO_2 Stack Gas Monitors

AeroVac, Troy, N.Y. produces the only known process type mass spectrometer that may be suitable for stack gas analysis. AeroVac proposes to utilize a Teflon membrane to separate SO_2 from the flue gas. As the instrument was under development and not commercially available, it was recommended that no additional evaluation be conducted until the vendor had the monitor ready for marketing. It was strongly urged that a laboratory evaluation of the dilution system, potential interferences and overall performance be performed on an off-the-shelf production unit when one becomes available.

Gas Chromatographic (GC) SO_2 Monitors

This class of instruments, at the time, had questionable utility as a stack gas monitor for SO_2. With the information available, it was not possible to recommend that a GC be included in the test program; however, the status of G.C. systems will be monitored for any significant change.

Gas Chromatograph (G.C.) - Evaluation of commercially available process G.C. systems was not appropriate at the time as the critical factors of sample pretreatment, automatic sample injection, column and materials technology to prevent spurious reactions and reliable analyses were not proven for this application. To date only one user (utilizing nonvendor supplied technology) reported satisfactory results.

Electrochemical Instruments (Attachment D-2)

Numerous electrochemical instruments were available on the market for the purpose of monitoring SO_2. Of these, at least 6 systems were recommended by their manufacturers for stack monitoring applications as opposed to ambient air monitoring. In the detailed evaluation presented in Attachment D-2, the principles of operations and potential interferences for conductometric, coulometric and fuel cell instruments are discussed.

Conductometric Instruments were ranked as follows:

1. Mitrogas-MSK-SO_2E_1 (Calibrated Instruments)
2. Scientific Industries Model 70 (they sell their own air dilution system)

Interferences in the above systems can be caused by NO_x and other stack gas constituents. Reaction kinetics and catalysts which may be present could pose application limitations.

Coulometric Instruments were ranked as follows:

1. ITT Barton Model 286
2. Beckman Model 906A (a Teflon membrane is utilized for SO_2 separation and dilution). It is to be expected that No_2, etc. will interfere to some extent. The Beckman instrument is basically an air monitor and had not been tested on combustion stacks.

Galvanic or Fuel Cell Type Detectors - Dynasciences and EnviroMetrics offered SO_2 analyzers. These units are small, compact and appear to be easy to operate. User reports indicated the analyzers do not have the expected long term reliability apparently because of cell poisoning.

As a result of the Task D "evaluation," the following equipment was selected for inclusion in the test program. The major criteria was: did a specific piece of equipment best typify a given analysis method or technique?

TABLE D-1

Equipment Selected for Field Testing

Manufacturer	Model	Technique
Dynasciences	SS330	Electrochemical - "fuel cell"
Calibrated Instruments	MSK-SO_2-E_1	Electrochemical - conductometric
ITT Barton	400	Electrochemical - coulometric
Bendix	UNOR 6	NDIR "new type detector"
Intertech	URAS-2	NDIR
DuPont	460	Ultra violet absorption
Melloy Labs	prototype	Flame photometric detector

The decision not to include several other instruments or manufacturers was generally based on delivery times (Beckman, Environmental Data Systems), cost or duplication of other techniques.

APPENDIX D-1

NDIR INSTRUMENTATION FOR STACK GAS MONITORING

1. Introduction

This report summarizes the results of a study of five non-dispersive infrared (NDIR) SO_2 monitors. The devices were designed to continuously monitor the concentration of SO_2 in stack gases from coal burning power plants. All units use as their principle means of detecting SO_2 the selective absorption of infrared radiation by SO_2 molecules, and consist of an IR source, a chopper, a sample chamber, a reference chamber, and a detector unit.

The radiation from the source traverses the sample chamber and the reference chamber. Beneath each chamber is a sealed unit filled with SO_2 gas; a thin diaphram separates the unit beneath the reference chamber from that beneath the sample chamber. When no SO_2 is in the sample chamber, equal amounts of energy are absorbed by the SO_2 gas in each unit. When SO_2 gas is introduced into the sample chamber, it absorbs energy, and more energy enters the chamber beneath the reference cell, creating a pressure differential which is detected by the diaphram.

2. Units Under Consideration

The units considered were:

1) Leeds and Northrop - IR gas analyzer
2) Bendix Unor
3) Intertech Uras
4) Beckman Model 315A
5) MSA - Lira Model 300

Unit number 1, although of a potentially superior design, has been withdrawn from the market by the manufacturer and will not be discussed further. All of the remaining units were of a two cell, electro pneumatic type.

3. Features Common to All Detectors

All of the units suffer from problems associated with the method of detection.

3.1 Fly Ash and Particulate Matter -

The manufacturers of all units require that the gas sample be filtered to remove fly-ash and particulate matter. This is because the measurement to be made is an absorption measurement, and any thing which reduces transmission gives a positive indication of SO_2.

In addition, it is clear that particulate matter collecting in the windows of the sample cell in a two-cell system will introduce a systematic error into the reading. At the same time, it will decrease the signal to noise ratio and therefore, affect the accuracy of the measurement.

Hence the degree to which NDIR detectors will be useful depends critically upon the filtrations system ability to uniformly and consistently remove particulates from the sample.

3.2 Water Vapor -

All of the instruments under discussion work on the principle of absorption of radiation by SO_2 in the sample gas. The primary SO_2 absorption band in the 1400 cm^{-1} region is overlapped by a water system which exists in the 1200 cm^{-1} to 2000 cm^{-1} regions. Hence, water vapor in the system will effect the measurements and therefore must be removed from the sample or be a known quantity. A method suggested by most manufacturers involves the use of a cold trap held at 0°C. This has two effects: it removes a large percentage of

the water vapor and in principle at least, the remaining water vapor content is known and can be accounted for in the measurement. This is not as straight forward as it appears, however, since the design of the cold trap is all important to the efficiency with which the water vapor is removed. In addition, the vapor pressure of water at 0°C is 4.6 torr or about 6000 ppm. Variations in the temperature of ± 1°C result in changes in the vapor pressure of ± 0.3 torr or about 400 ppm. Since we are concerned here with SO_2 concentrations in the order of 200 to 1000 ppm, we not only require that the temperature be held very constant in the trap but that the rejection ratio of H_2O over SO_2 by the detector must be very high if the measurements are to be valid. Beckman indicates that the rejection ratio for their detector is 100:1, i.e., 100 ppm H_2O gives the same signal as 1 ppm SO_2. If this is representative for the other detectors then an efficient trap held at 0 ± 1°C will be sufficient, as this will result in an error of ± 4 ppm SO_2, which is about the required sensitivity of the instrument.

An additional problem exists with respect to water vapor. At 0°C, the solubility of SO_2 in water is very high, being about 22.8 gms/100 cc. This means that SO_2 will be taken out of the gas when the water is removed. The amount of SO_2 removed cannot be calculated but must be measured, as it depends upon the trap design, flow rates, amount of precipitable water present, etc.

The purpose of this report is to discuss the NDIR detectors, and the consideration of cold trap design constitutes a digression which introduces a host of additional problems. Suffice it to say that it is a matter of concern for all such detectors, and unless a manufacturer can specifically demonstrate he has overcome the problem, the NDIR detectors discussed below are of questionable use as consistently accurate SO_2 monitors where a wide variation in water vapor concentration exists.

The methods used to compensate for water vapor in the instruments consists of positive filtering and negative filtering. In positive filtering, the radiation is prefiltered in the wavelength region of the interferent before traversing the sample and reference chambers. Removing radiation in the water band does reduce the sensitivity to water vapor but also affects the SO_2 sensitivity by reducing the amount of signal in the SO_2 band as well.

Negative filtering is done in various ways, but in one model (URAS2) SO_2 gas is introduced in the path of the radiation traversing the reference chamber. This primarily removes radiation from the center of the absorption band in the reference side[1] and the difference between the radiation in the center of the absorption band and the flanks is formed in the detection system. Such a system is less sensitive to interference from water vapor. If a known amount of water vapor is present, an additional filter is placed in the reference side which absorbs radiation equivalent to that absorbed by the water in the sample side.

3.3 Pressure and Temperature -

In all of the instruments discussed below, the degree of absorption is proportional to the total number of SO_2 molecules in the sample path. Assuming the volume then gives a calibration of concentration vs. signal level. However, changes in the ambient temperature and pressure will affect the readings. The errors introduced are 0.3% per °C change and 1.3% per 10 mm hg change. Most instruments compensate for changes in the barometric pressure and some for temperature. These are noted in the instrument discussion. No mention is made where the information was unavailable.

3.4 Microphonics -

All of the instruments discussed below are thermo pneumatic and are therefore subject to microphonics induced by vibration. In this respect it is important to test the instruments prior to use, as this is the only practical way of determining the soundness of design, care of construction, etc. of a unit.

3.5 Other Errors -

All of the instrument manufacturers recommend frequent recalibration using prepared sample gases with known SO_2 concentrations. Obviously then, all of the instruments are susceptible to calibration errors in direct proportion to the accuracy of the composition of the sample gases.

In addition, care in filling the detectors and contaminants introduced therein constitutes an error source to which all of the units are susceptible.

4. Discussion of Units

The units considered will be discussed below in the order in which they were ranked. The ranking was partially subjective in that it was done solely on the basis of design considerations. In those applications where one specification (e.g. low span drift) is desired above all others, a different ranking would result. In addition, a unit of potentially superior design is of no use if it is poorly constructed, has a low time between failures, is difficult to repair etc. Since the units were not available for test, no consideration could be given to these aspects. It is strongly recommended the units be tested prior to selection of one of them for on-site measurements. This will be discussed further in Section 5 below.

4.1 Bendix Unor -

This unit is shown schematically in Figure 1. It is a two chamber/two detector device which utilizes the fact that, for a

spectral absorption line with a Lorentz shape, the absorption coefficient is given by:

$$\varepsilon(\nu) = \frac{Pb}{\Pi[(\nu-\nu_o)^2 + b^2]}$$

where ν_o is the line center frequency, P is the power, and b is the half width. For radiation passing through a sample of gas, the energy in the center frequencies of the absorption line is preferentially absorbed over energy from the wings of the line. In the Unor the design is such that the center energy is mostly absorbed in the top detector, and the flank energy in the bottom.

With no SO_2 in the sample chamber, the absorbed energy is equal in both detectors. When SO_2 is introduced in the sample chamber, the center frequency energy is absorbed in the sample chamber instead of in the top chamber creating a pressure imbalance, and therefore a signal in the microphone.

This unit has some advantages over the remainder of the units in that it is less sensitive to broad band interference, since such interference affects the wings and center of the line, and therefore both detectors, equally.

It has a single IR source, in contrast to double IR sources of other units; this also is considered an advantage since there is just one less thing to malfunction during long periods of unattended operation.

For some reason, temperature compensation is not available with this unit, although pressure compensation is.

4.2 Intertech URAS (Figure 2) -

The main advantage of this unit over the remaining units is what appears to be flexibility in design. The manufacturers seem willing to alter the system quite drastically as might be necessary to suit the applications. It has capability of positive filtering for interferents, and, particularly for water

vapor problems, can be obtained set up with negative filtering.

In the latter case the detection technique is changed from a simple energy detector (depicted above) to a scheme similar to to Unor which depends upon preferential absorption of center frequencies of the absorption line. This is shown in Figure 3 below. Operation in this mode is not completely satisfactory, however, since in order to balance the two chambers, a neutral density filter (a wire mesh) must be inserted into the sample chamber path. This reduces the available energy and therefore decreases the signal/noise ratio.

4.3 Beckman 315A (Figure 4) -

This unit is a simple energy balance detector. It has a slightly wider range of temperature operation than the other units, in that it is capable of operation at temperatures ranging from -20 to +120°F.

The manufacturer recommends daily recalibrations, which is somewhat more frequent than other manufacturers; however, this may be due more to a lack of candor on the part of other manufacturers than to a lack of stability in this unit.

4.4 MSA Lira Model 300 (Figure 5) -

This unit is simply a UNOR scheme with a single chamber. The temperature range of operation of the unit is from +30 to +120°F, which may be inadequate for stack monitoring in colder climates. The smallest range of operation available off-the-shelf is 0-5000 ppm which is a bit gross for the measurements under consideration here. The manufacturer states that smaller ranges are available but there is no information as to cost, delivery times, effect of the change on the accuracy of the unit, etc.

The chopper frequency is 2 CPS, which is a bit low. The optimum chopper frequency for thermo-pneumatic detectors is about 10 to 15 CPS.[2]

And lastly, the electronics may be a bit outmoded, being of tube design rather than solid state. While tube designs can be made which are every bit as stable and capable of long MTBF as solid state designs, they usually are not. They also require more power and are more susceptible to heat problems.

In defense of the unit, it appears to work under actual conditions. The unit has been in service for years, is very rugged and is apparently reliable. In the final analysis this may be the qualifying factor and the MSA unit may prove to be superior to the other units which, although of potentially superior design, may not in fact deliver that superiority in the finished product.

5. Recommendations and Conclusions

It is strongly recommended that a laboratory program be carried out to test these instruments prior to selection of one of them for stack installation. There is no way of determining the care of circuit design, ruggedness of construction, reliability, and susceptibility to interference by reading the manufacturer's literature. As stated above in the discussion of the MSA unit, shoddy workmanship or poor design can easily negate the minor inherent advantages possessed by units such as the Unor.

Such a program need not be extensive. The minimum test program should probably include the following:

1) Turn units on and measure zero drift as a function of time. If environmental chambers are available, drift can be checked as a function of temperature and pressure variation.

2) Test sensitivity and reproducibility of SO_2 measurement using sample gases of known composition over the range of operation of the instruments.

3) Tests to determine the effects of water vapor on the measurement.

Item 1 (without the environmental test equipment) and Item 2 require almost no special laboratory equipment and can be done at very little cost. The cost and time involved in Item 3 is as little or as great as desired, since a simple experiment would suffice in giving a rough idea of the effect of water vapor on the SO_2 measurement. For example, SO_2 gas of known concentration in dry air can be run through a detector. The same gas is then passed over a water reservoir held at known temperature (and therefore vapor pressure), the wet gas run through the detector, and the resultant measurement compared with the previous one. This is a crude measurement but it can be performed on all of the instruments uniformly and the instrument response noted. Any differences in the ability of the instruments to reject water vapor interference should show up immediately.

If more time and money are available, more elaborate schemes could be carried out wherein the water vapor content is accurately measured before and after the gas is run through cold traps and the effects on the measurements noted.

6. Conclusions

A survey has been made of five instruments designed to measure SO_2 concentrations in stack gases of coal burning power plants. The instruments have been ranked according to design. All such instruments, generally called NDIR detectors, are only conditionally suitable for use as continuous monitors since all suffer interference from particulate matter, water vapor and vibration.

It is concluded that the proper ranking of the instruments can only be done after the instruments have been subjected to laboratory tests to measure their performance.

Figure D1-1

Bendix Corporation UNOR-2 Infrared Analyzer

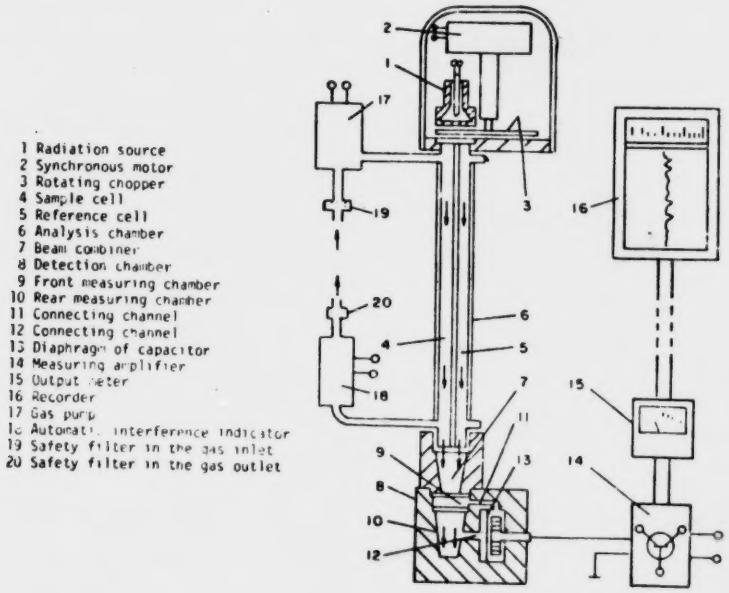
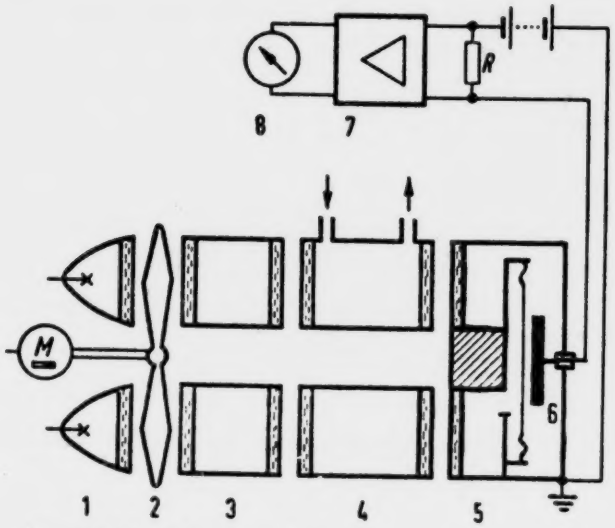


Figure D1-2

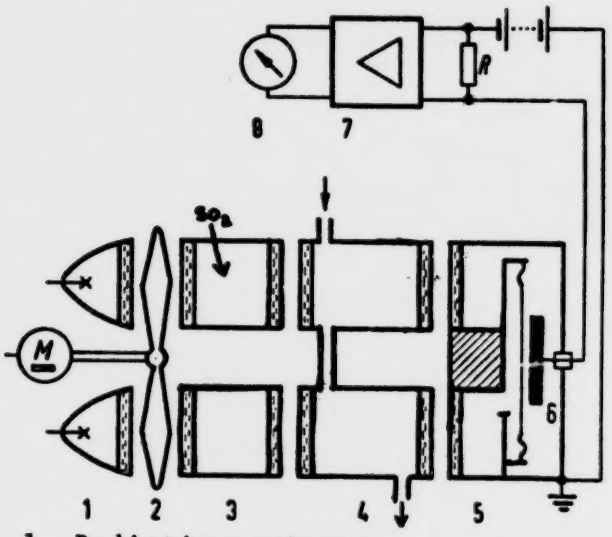
Intertech URAS-2 Infrared Analyzer



1 Radiation emitter
2 Mechanical chopper
3 Filter
4 Measuring gas cells (top: sample cell, bottom: reference cell)
5 Sensor
6 Capacitance-type detector
7 Amplifier
8 Meter or recorder

Figure D1-3

Intertech URAS-2 In The Negative Filter Mode



1 Radiation emitter
2 Mechanical chopper
3 Filter
4 Measuring gas cells

5 Sensor
6 Capacitance-type detector
7 Amplifier
8 Meter or recorder

Figure D1-4

Beckman Model 315A Infrared Analyzer

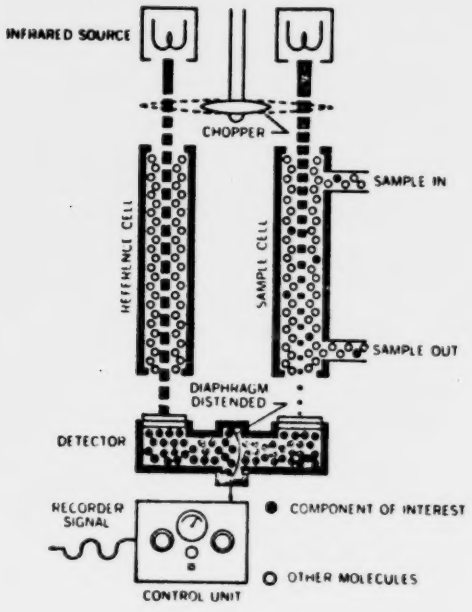
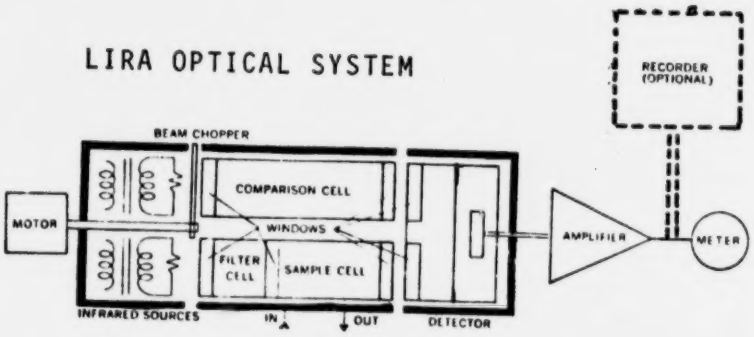


Figure D1-5

Mine Safety Appliances LIRA Model 200



Figures D1-1 through D1-5 from "Instrumentation for Determination of Nitrogen Oxides Content of Stationary Source Emissions," APTD PB 204877, Volume I, February 1972.

APPENDIX D-2

ELECTROCHEMICAL INSTRUMENTS FOR MONITORING SO_2 IN STACK GASES

Prepared By

R. R. Sayano
E. T. Seo

Science Staff
Chemistry and Chemical Engineering Laboratory

December 1970

1. INTRODUCTION

Commercially available SO_2 analyzers based on the use of electrochemical principles were evaluated for use in continuous monitoring of SO_2 in stack gases. The primary requirement was for "off-the-shelf" instruments capable of continuous in-stack monitoring at coal- or oil-fired stack gases containing 200-700 ppm SO_2 (but with a range extendable to 3000 ppm SO_2). The evaluation included a review of: basic electrochemical principles involved, theoretical and practical limitations, possible interference from other stack gas constituents, operating procedures, maintainability, and physical construction. A tentative criteria for selection and further evaluation were established and instruments rated according to the criteria. Recommendations for modifications and/or improvements of these instruments were also considered.

The instruments were of the following three types: conductimetric, coulometric, and "fuel cell." Following instruments were evaluated:

Conductimetric:

Mikrogas-MSK-SO_2-E_1	Calibrated Instruments.
Model 70 Stack Monitoring System	Scientific Industries
Series 11-7000 Series SO_2 Air Pollution Monitor	Davis Instruments
Series 9000 PPM Gas Analyzer Systems	Devco Engineering Inc.
Model 902	Instrument Development Co.

Coulometric:

Model 286 Recording Sulfur Titrator	ITT Barton
Model 906A Diffusion Stack Monitor	Beckman Instruments, Inc.
DW9700 SO_2 Monitor	Phillips Electronic Instruments
Model 200 Iodometric SO_2 Analyzer	Atlas Electric Devices Co.
Titrilog II	Process Analyzers Inc.

"Fuel Cell"

Series NS-200 Multigas Analyzer	EnviroMetrics Inc.
Model SS-330	Dynasciences

In all these analyzers, the SO_2 gas passed into water or a reagent solution where it either is converted to an ionically conducting species, reacts with a coulometrically generated titrant, or reacts at an electrode.

Since electrical measurements can be made with great accuracy, sensitivity, reproducibility, and relative ease, the amount of SO_2 detected can be very low if the technique is specific to SO_2. Detection at the 10^{-10} molar level is achieved with present day electrochemi al techniques. In addition, the electrical signals are amenable to remote control and signal processing techniques. The overall construction of electrochemical systems are usually simple, and can be made small and often portable.

Theoretically by the proper selection of electrolytes and electrochemical conditions, the detection system can be made highly selective and sensitive to a specific species with response time within a fraction of a second.

In reality, the procedures encounter difficulty because of sample handling, low rates of reaction, and lack of specificity. Drawbacks of the instruments evaluated in this study are:

conductimetric

- sample gas must be passed into deionized water or H_2O_2 solution to give an ionically conductive solution
- other constituents of stack gases can form interfering ionic species
- reagent (viz., H_2O_2) concentration changes due to depletion or evaporation
- temperature changes affect conductivity and reaction rates (requires well thermostated cell)

coulometric

- sample gas must be passed into electrogenerated titrant solution for reaction,
- reagent lost through evaporation
- temperature changes affect electrode potential and reaction rates
- any other constituent of stack gas that can undergo oxidation or reduction in coulometry cell will cause interference

"fuel cell"

- sample gas must pass through membrane (increases response time)
- temperature effects electrode process and diffusion rate
- membrane characteristics changes with time and changes in environment
- reagents within fuel cell become depleted
- nonspecificity of membrane to SO_2 causes interference

2. SELECTION AND EVALUATION CRITERIA

Commercially available SO_2 analyzers (air monitoring instruments) based on electrochemical techniques were evaluated for use in continuous in-stack monitoring of SO_2. Primary emphasis was placed on "off-the-shelf" units capable of monitoring SO_2 in the range 200-700 ppm. If a gas sampling or conditioning unit for adapting an air monitoring instrument for stack-gas use was not available as standard equipment, the instrument was not rated as a candidate. Such an instrument may be useable later when modifications or stack gas sampling are made available. Information required for preliminary selection and evaluation was obtained from a basic understanding of an instruments operating characteristics, manufacturer specification sheets and instruction manuals, or by direct contact with a manufacturer's representative.

The following parameters were established as possible criteria for further evaluation of the instruments. The nominal values given are those required or can be met by the unit.

Range: overall dynamic range for SO_2 detection (nominally 200-700 ppm)

Accuracy: percentage (or ppm) variation from known standard (nominally ±5% of full scale)

Zero Drift: variation in output with time for zero SO_2 input (nominally less than 3% per day)

Span Drift: variation in output with time for constant SO_2 input

Response Time: time required for output to reach 90% steady state value for step change in SO_2 (nominally 20 sec to 5 min)

Lag Time: time required for first detectable output for step change in SO_2

Ambient Condition: operating condition of total unit (nominally temperature 32 to 100 °F, relative humitity, R.H., 0 to 100%)

Flow Rate: sample gas flow rate to analyzer

Interference: percentage (or ppm) change in SO_2 reading caused by possible interfering species present in equal amount as SO_2

Sensitivity: minimum detectable level of SO_2 (nominally less than 2% full scale)

Electronic Drift: output drift with time with zero SO_2 input attributable to electronic system (nominally negligible compared to zero or span drift)

Maintenance Cycle: period of unattendent operation of unit before manual maintenance is required (nominally 3 mo)

3. CONDUCTIMETRIC INSTRUMENTS

Conductimetric instruments measure the change in conductivity of a solution resulting from the addition of SO_2. In some instruments, SO_2 is simply dissolved in deionized water and the increase in conductivity of the solution is due to the reaction

$$SO_2 + H_2O = H_2SO_3 = H^+ + HSO_3^-$$

Other instruments use a solution of H_2O_2 which oxidizes SO_2 (or H_2SO_3) to the more highly ionized sulfuric acid.

The increase in solution conductivity in either case is directly proportional to the amount of SO_2 in the sample gas. Schematically, the sample gas is continuously exposed to deionized water or the H_2O_2 solution which then flows into the measuring cell consisting of two fixed-geometry inert electrodes separated by a fixed distance. Flow rate of the solution is set so that all the SO_2 is equilibrated or reacted before entering the measuring (conductivity) cell. To prevent polarization of the electrode, alternating current is used and the conductance is measured using a bridge circuit. Stable readings are obtained if the cell is maintained at constant temperature (e.g., 20 °C) or if a temperature compensation circuit is used. The spent solution is either dumped into a holding tank or recycled after it is passed through deionization columns. In the case where deionized water is used (no H_2O_2), CO_2 can cause interference. Correction for the CO_2 interference is made by measuring the conductance of a SO_2-free sample gas. In addition NO_x can (thermodynamically) react with water to yield HNO_3, a strong acid. However, the rates of such reactions is probably slow enough that the interference is small. Instruments capable of monitoring SO_2 in stack gases are:

Mikrogas-MSK-SO_2-E_1	Calibrated Instruments
Model 70 Stack Monitoring System	Scientific Industries

4. COULOMETRIC INSTRUMENTS

Coulometric instruments are based on the principle of coulometric titration where electrogenerated halogen (bromine or iodine) serves as the titrant. Basically, the measuring cell contains, for example, an aqueous solution of Br^- and Br_2. A fixed Br_2/Br^- ratio establishes a constant potential at an indicator electrode. When SO_2 is introduced,

$$SO_2 + Br_2 + 2H_2O \longrightarrow H_2SO_4 + 2H^+ + 2Br^-$$

The concentration of Br_2 decreases, causing a shift in potential. This potential shift is detected and current is supplied to a pair of generating electrodes to re-establish the initial Br_2 concentration. The current required in the process is proportional to the amount of SO_2 in sample gas. Since the role of SO_2 is to cause a change in Br_2 concentration by reduction, any other species present in stack gas which either oxidizes Br^- or reduces Br_2 will interfere with the SO_2 readings. For example, if NO and NO_2 are present with SO_2, the formation of HNO_2 is thermodynamically favored and HNO_2 can be reduced by iodide or SO_2. Once again, since the rates of these reactions are probably low, the extent of interference could be small. The nominal interference due to NO_2 (where the concentration of NO_2 = SO_2 = 1 ppm) is reported to be less than 5%. Even when the NO_2 and SO_2 concentrations are about 300 ppm each, preliminary tests (telecon with ITT Barton) have shown that the interference is less than 10%.

Off-the-shelf instruments recommended for possible use in stack-gas monitoring are:

Model 286 / or 400	ITT Barton
Diffusion Stack Monitor Model 906A	Beckman Instruments

Other instruments considered were:

PW 9700	Phillips
Model 200	Atlas Electric Devices
Titrilog II	Process Analyzer Inc.

5. "FUEL CELL" INSTRUMENTS

The "fuel cell"-type instruments are based on a completely sealed sensor functioning as an electrochemical transducer. Basically, the SO_2 diffuses through a membrane and dissolves in a thin layer of electrolyte. An oxidation or reduction occurs at the sensing electrode, resulting in a current which flows to the counter electrode through an external load. The amount of current indicates the SO_2 content of the sample gas. Some of the drawbacks of this type of instrument are:

- Membrane is not highly specific to SO_2 (NO_2 is a major interfering species); and
- Membrane surface must be kept free of condensate and particulates.

In one unit (Environmetric Inc.), the NO_2 interference is subtracted from the total "SO_2" reading by using an additional sensor which responds only to NO_2. However, this requires continuous calibration of two sensors and that both sensors to be operative at all times.

6. FUTURE WORK

From this preliminary study in the selection and evaluation of electrochemical monitoring instruments for stack gas SO_2, future work in the following areas is recommended:

- Examine the rates of chemical reactions involving interfering species and develop procedures that take advantage of reaction rate differences to minimize the effect of the interfering species.
- Laboratory testing of selected instruments using simulated stack-gas conditions to establish quantitative criteria for actual in-stack evaluation; and
- Design of gas sampling or conditioning system for isolating SO_2 from interfering species in stack gas.

TASK E

Design of Test Procedures and Experimental Plan

The design of hardware, operating procedure and test plans will be discussed under the following categories:

Sampling Manifolds - These include probes, heavy particulate filters, main heat traced transfer lines, mixing zone (to insure homogeneous gas stream) common sampling point for individual transfer lines to each instrument. Initially Intertech probes were installed in the duct between the dust collector and the stack (of Unit 1, Moapa Power Plant). Dekoron or a similar type of heat traced Teflon tubing was planned to be initially utilized as transfer lines. The final design of the transfer system (line sizes, number of filters, etc.) was determined after the instruments are selected, filters tested and required flow rates determined. Evaluation of at least two types of particulate filters was planned. These include Intertech carborundum and Western Precipitation fiberglass types.

Manuals for the following instruments and equipment have been assembled.

Supplier	Manual
Bendix IR215 for CO	General operation manual
Intertech Corp.	Self balancing CMR converter
	Electronic temperature controller
	Operating manual for URAS-2 SO_2 analyzer
Westinghouse	Operating instructions for oxygen analyzer
DuPont	Temporary instruction manual for 460 SO_2 analyzer
Dynasciences	Operating instructions for air pollution monitor

Supplier	Manual
Calibrated Instruments	Operating instructions for MSK-SO_2-E_1
Bendix UNOR-2	Installation and operating instructions
	Servicing instructions
Barton ITT	Training manual

The above manuals will be used for:

Installation procedures

Calibration procedures

Operation and maintenance information

Flue Gas Velocity Mapping - Figures E-1 through E-3 illustrate the originally proposed probe assembly and method of probe introduction. By utilizing the instruments provided in the Intertech trailer, SO_2, CO_2 and O_2 could be concurrently determined while performing the velocity traverse.

Calibration System - Figure E-4 is a sketch of the originally proposed calibration and back flush systems. As illustrated individual instruments could be manually calibrated and an electronically controlled zero-span check system would operate through a common sampling point manifold.

Sampling System - Figures E-5 and E-6 represent the Intertech probe and filter assembly and one approach to sampling "on-the-stack," respectively.

Sampling System

An alternative sampling system was suggested for consideration by the EPA Project Officer in which a large volume or portion of the flue gas could be diverted to the trailer. Figure E-7 is illustrative of such a system. This system was considered for inclusion and has the following advantages and disadvantages on Unit 1 of the MOAPA site.

Advantages -

a) easy to install probe for each instrument

b) ease of checking and replacing filters

c) high velocity fan would provide excellent mixing and uniform sample in manifold

d) sampling conditions could be modified with relative ease

e) technicians and engineers do not have to leave ground level to service system, install or change filters, etc.

f) all of the system, excluding bracing and blower, can be obtained locally

g) short sample lines to instruments could be used

Disadvantages -

a) a high horsepower, efficient blower is required to insure that velocity in the pipes and manifold are sufficiently high to insure that particular build-up is minimized

b) a blower suitable for high dust loading and capable of producing necessary pressure increase for the desired high flow rates would require 4 to 6 weeks delivery time

c) the transfer pipe would require additional external supporting to insure structural strength to withstand the high velocity gusts of desert winds

d) particulate buildup could be a potential problem if there were any stagnant points in the transfer system

e) the zero and span check systems are more complex

After consideration of these disadvantages, the TRW staff decided to use the primary approach illustrated in Figures E-5 and E-6.

Sample Conditioning Systems - Sample conditioning systems are those pieces of hardware and equipment that are necessary for preparing and/or modifying stack gas physical or chemical characteristics prior to introduction into specific instruments. This equipment included any required pumps, filters, moisture removal traps, etc. The following instruments required preconditioning or pretreatment systems as per vendor specifications.

UV-VIS DuPont Model 460 - This system came complete with the necessary sample pretreatment equipment which is comprised of heated lines and cell, negative pressure regulation and air aspirated pump.

NDIR - In general this class of instruments required efficient small particle filtration, water removal, sulfuric acid demisting and pumping.

Electro-analytical - The galvanic cell type instruments (Dynasciences and EnviroMetrics) required reduction in the water content of the gas, fine particle filtration and pumping. The coulometric and conductometric instruments required that the gas stream be cooled and maintained at a precise flow using an ambient heat exchanger and pump/regulator equipment. These instruments may suffer from interferences by other species in the gas stream. If the vendor provides specific pretreatment equipment to eliminate interference, the equipment was incorporated in the sample conditioning system.

Calibration Systems - Two types of calibration were planned. These include standard systems for individual instruments and a drift check system where zero and 800 ppm SO_2 gases were sequentially introduced at the common sampling point manifold, thus allowing a simultaneous check of all instrument operation on the manifold.

Initial Data Acquisition and Test Plan

The operational procedures for the various instruments to be tested were those provided by the instrument vendors.

The following initial plan for data acquisition was planned to permit acquisition of meaningful and adequate data for the statistical evaluation of each instruments' performance compared to each other for ranking and to the criteria specified in Task B.

Accuracy - initially duplicate, parallel trap systems will be operated a minimum of five* time/day, during first three weeks, on the order of three days/week (90 tests). This number will be reduced for the duration of the program to once/week and three times/day if adequate.

Data rate for instruments during the accuracy test will be 30 sec. per instrument (if changes in concentration cannot adequately be followed by this data rate, it will be increased -- conversely, if changes are sluggish data rate can be decreased.)

Precision-Reproducibility-Response Time - these are all determined from zero drift-span drift and linearity calibration tests. Zero and span drift will be run daily and calibration weekly; all data points will be obtained in triplicate on a random basis.

Selectivity - specificity will be determined in the accuracy test but in addition, variations SO_2 values will be correlated with changes in CO, CO_2, O_2, power, etc. in plant. The EPA supplied trailer contained equipment for SO_2, CO, CO_2 and O_2 measurements on a continuous basis.

Standard Daily Operation - for the remaining criteria tests of environmental effects, maintenance reliability, etc. the instruments will be operated continuously but at a slower data acquisition rate.

The test procedure and experimental plan was reviewed at the 21 May project meeting. The plan remained as previously discussed except for the following changes.

Routine Data Collection - Data on all instruments will be collected every two hours. This data collection will consist of

---

*In order to detect a $2\bar{\sigma}$ change between sample means at 90% confidence, a minimum sample size of 4 points is required. A population of five was chosen to provide a margin which will permit discarding of an outlier.

10 data points for each instrument and will be collected at the maximum rate of the Esterline-Angus data acquisition printer (2.5 channels/sec).

Zero-Span - Zero and span checks will either closely precede or follow as many as practical of the above 2 hr. data collection periods. The data rate for this phase of the test will remain at a slower rate for longer periods of time to ensure that individual instrument responses and other important factors are recorded.

These changes were manually initiated and the procedure was later automated. An external trigger timer and relay system was installed for each of the above modifications. Esterline-Angus provided recommendations on timers and the proper integration with the printer.

The computer program MONSO$_2$ was written in CDC Fortran IV to provide a historical data storage and retrieval and statistical analysis capability for the SO$_2$ Monitor calibration data. The program is designed to accept as input the following information: date, times, millivolt (ADC) readings and gauge readings for the zero, span and calibration data and to add these data to a file containing past information. The retrieval and analysis function included the ability to list a particular date's results or each date's results (the individual data points), the ability to compute mean and standard deviations for any, each, or all calibrations, and the ability to compute linear or log linear calibration parameters and associated errors for any, each, or all calibrations.

Evaluation of Referee Wet Analysis Methods

A brief eveluation of three fundamental wet analysis procedures for quantitative determination of SO$_2$ in flue gas was completed in TRW's laboratory, i.e. 1) precipitation titration with barium, 2) colorimetric measurement utilizing barium chloranilate, and

3) acidimetric titration with standard base. The precipitation titration utilizes barium perchlorate titrant with the end point detection being visual (both thorin and Sulfanazo III indicators are being evaluated, as well as a specific ion electrode technique).

Nonetheless, difficulties with end point detection will significantly impact accuracy evaluation and consequently the study of other methods of end point detection. The colorimetric method which eliminates the major drawback of the titrimetric method is based on the original work of Bercolacini and Barney at Standard Oil Co. of Indiana (A.C. Vol. 29, No. 2, February 1957). It is not as desirable as the titrimetric from the standpoint of speed and ease of analysis. The third method is the acidimetric method of Berk and Burdick developed at the Bureau of Mines and has been included only for laboratory evaluation and comparison where acidic interferences will not be encountered.

A discussion of the experiments that were conducted and results are attached as Appendix E-1. To summarize, the results indicated that the barium perchlorate titration with thorin indicator yields slightly better accuracy and precision than does the same titration with Sulfanazo III. Nonetheless the three operators in TRW's laboratory expressed the (unwarranted) opinion that the Sulfanazo III end point was easier to detect. The barium chloranilate colorimetric method may be suitable for routine laboratory usage, however, because of the time required for sample work-up it was not used in the field test phase of this program.

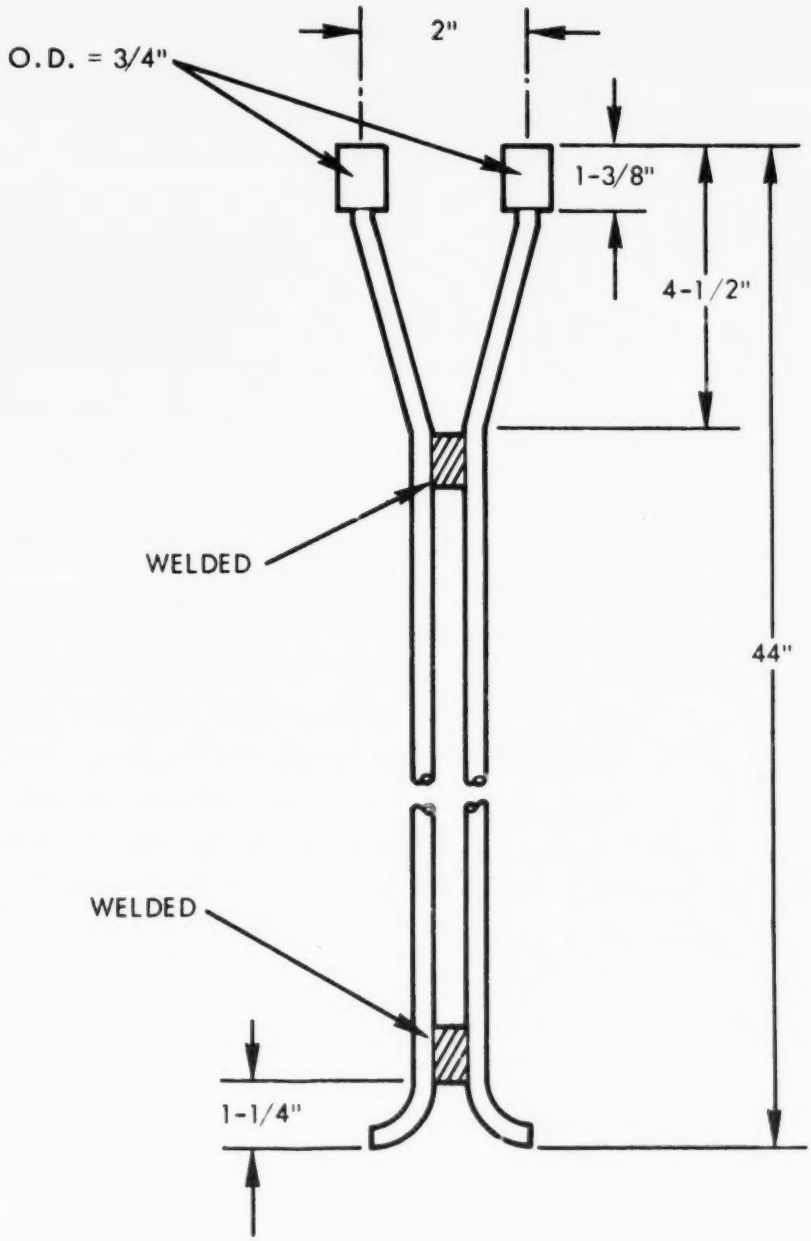


Figure 6-1 High Particulate Loading Velocity Mapping Probe

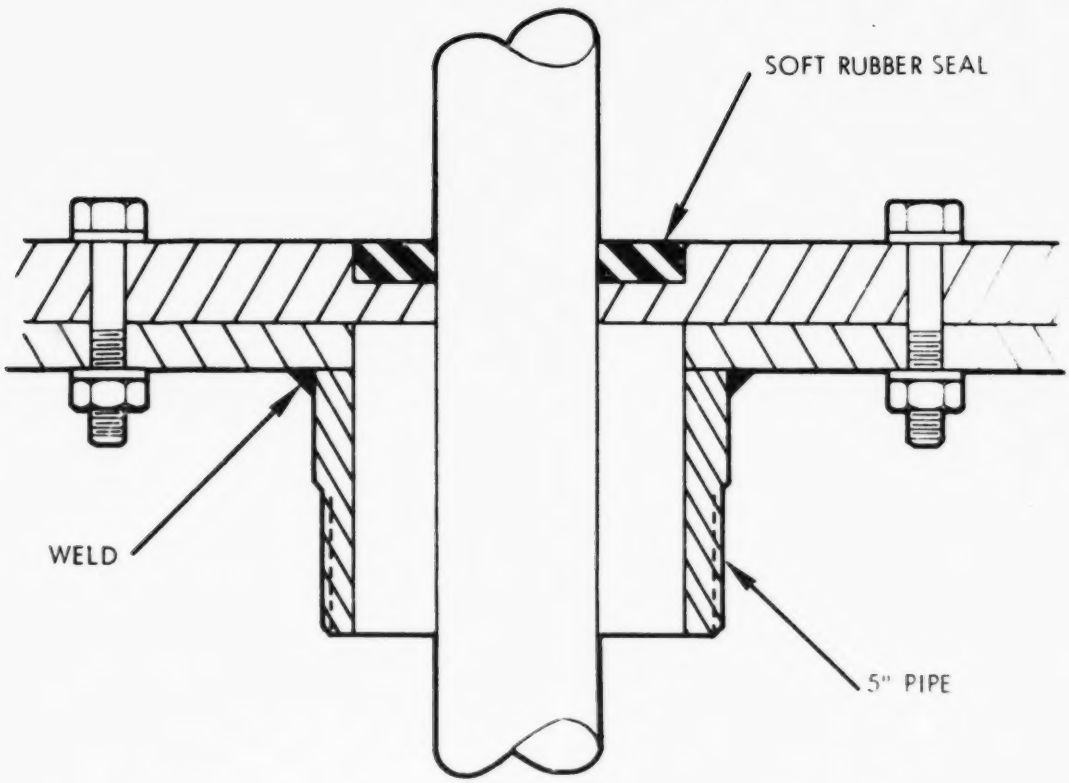


Figure B-1 Details of Gasket Assembly for Mapping Stack Gas

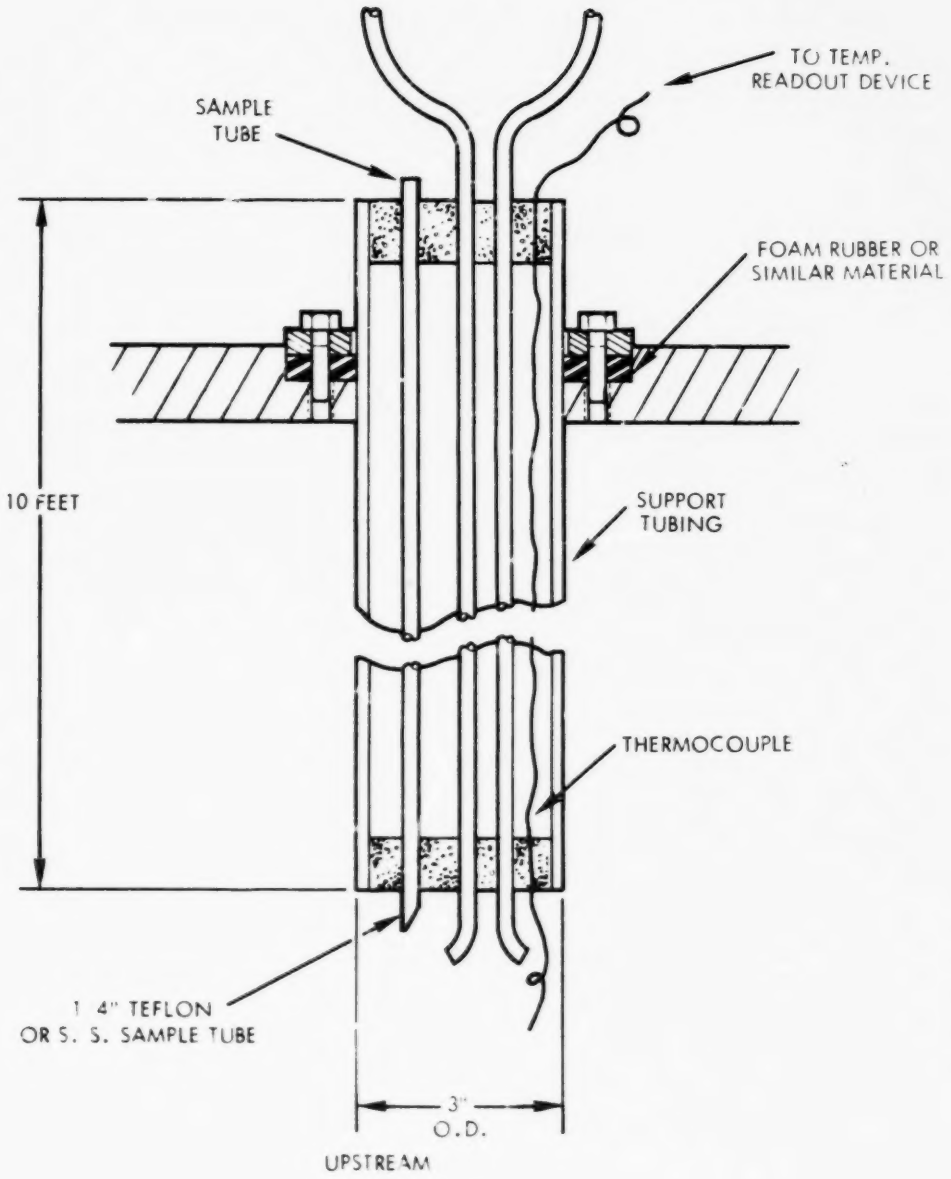


Figure E-3 Details of Integrated Flue Gas Mapping Probe

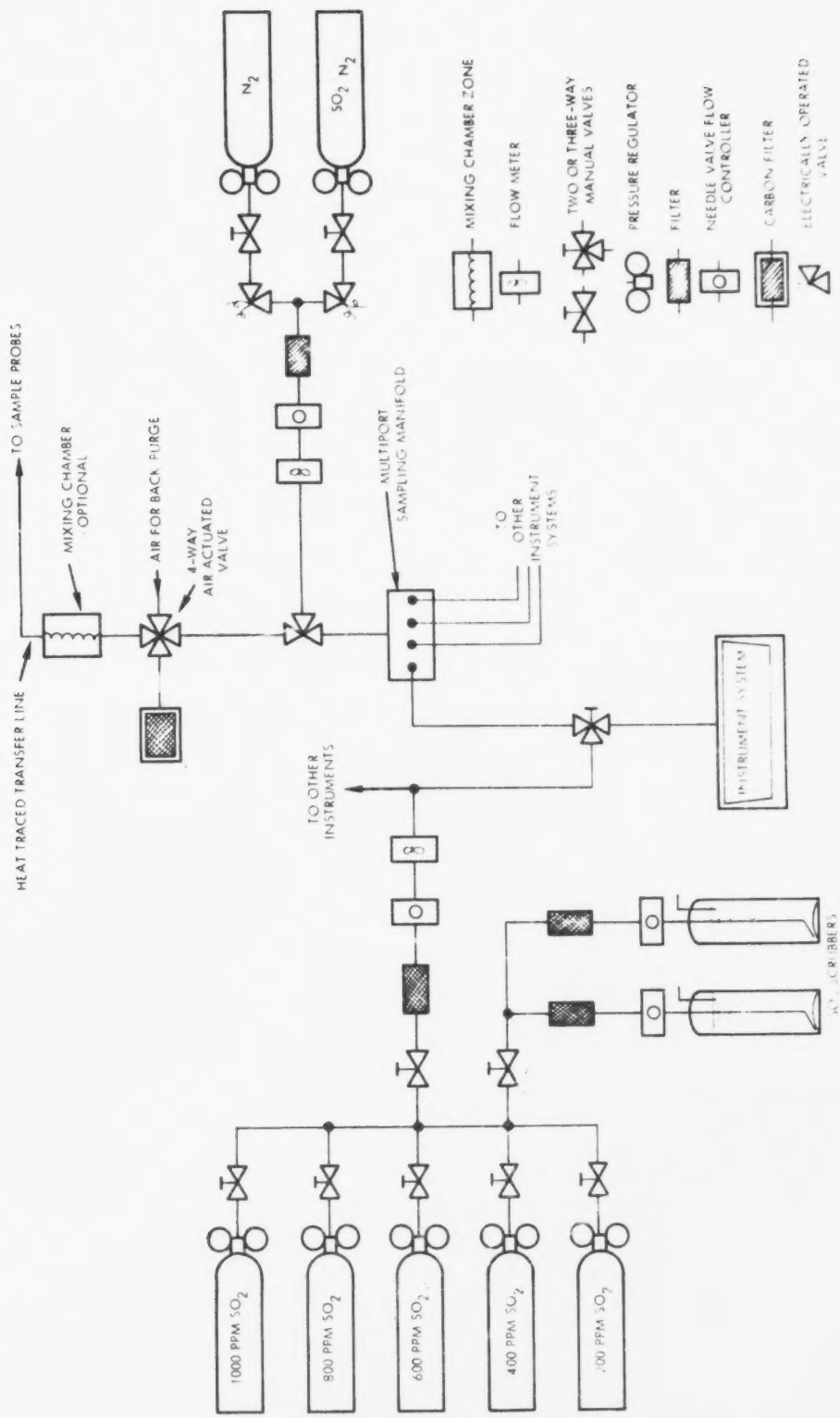


Figure E-4 Proposed Calibration and Backpurge Systems

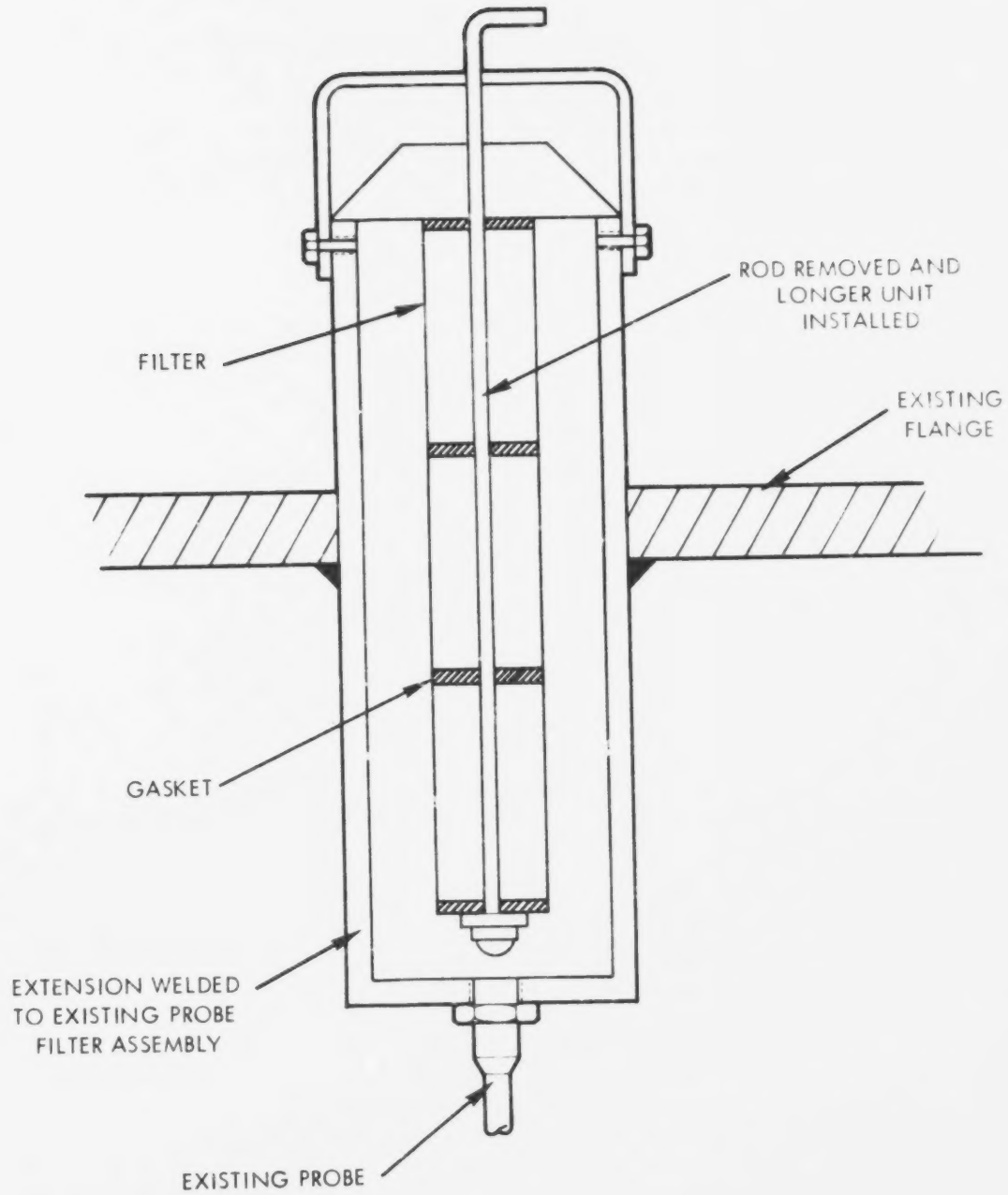


Figure E-5 Modified Intertech Filter Assembly

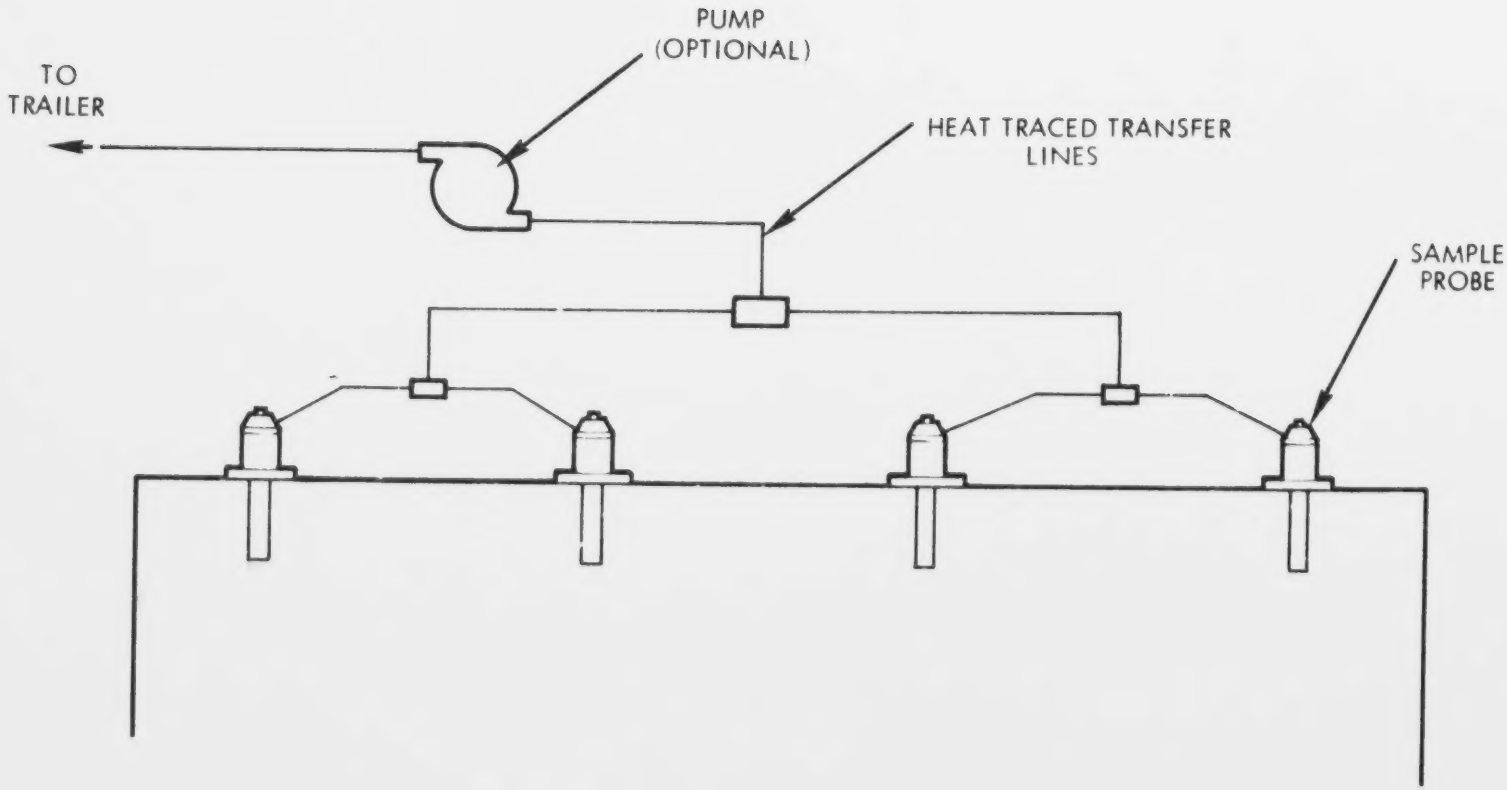


Figure ~~E-6~~ Sample Probe Installation "On-Stack"

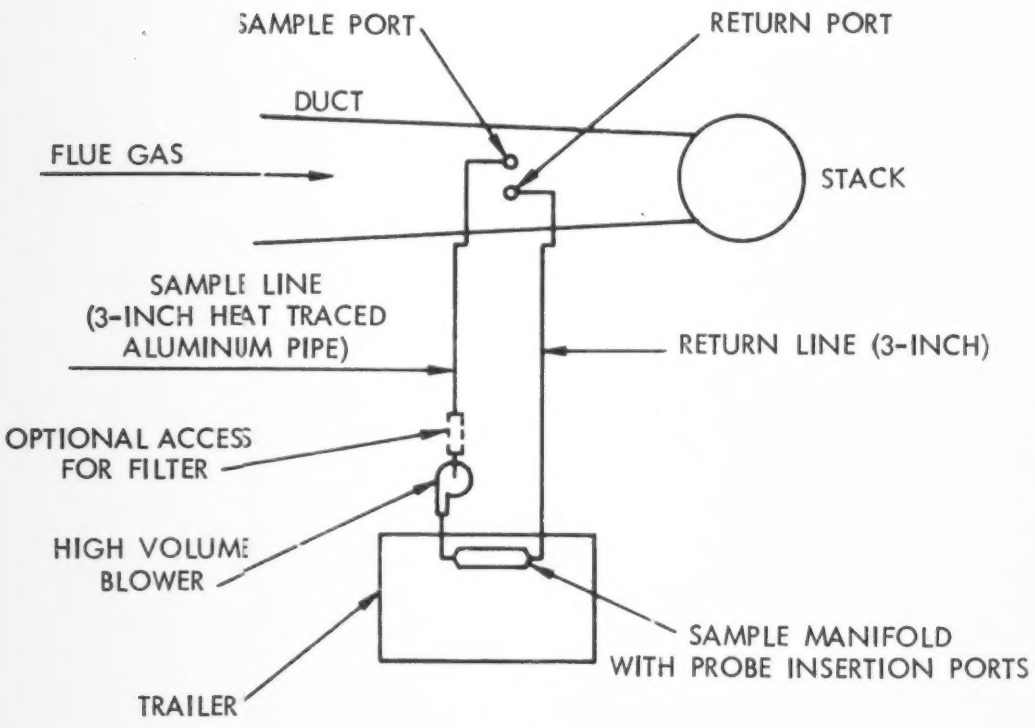


FIGURE E-7 OPTIONAL FLUE GAS DIVERSION SYSTEM

APPENDIX E-1

PRELIMINARY SULFUR DIOXIDE ANALYSIS METHODS EVALUATION*

INTRODUCTION

The tests described in this report were conducted in order to select a referee wet method for SO_2 to be used in a field test of SO_2 monitoring instrumentation for stack gas analysis. The gas sampling apparatus shown in Figure 1 was assembled and utilized in the laboratory tests so that sampling parameters would be considered as well as the analytical test procedures in the evaluation. The barium perchlorate titrimetric method utilizing Sulfanazo III and thorin as visual end points, an acid-base titrimetric method and the barium chloranilate colorimetric method were evaluated.

Instructions for analysis of sulfate using the barium perchlorate-thorin method were taken from the Shell method, while the procedure for sulfate analysis by barium chloranilate was that proposed by Bertolacini and Barney[1] and modified by Kanno.[2]

The upper range that was examined by other investigators for the thorin method was 6000 ppm as sulfur dioxide, while the lower limit was 25 ppm. The useful and linear concentration range given by Bertolacini and Barney[1] for the chloranilate method is 1 µg/ml as sulfate in the solution measured in a 5 cm cell to 400 µg/ml in a 1 cm cell. Kanno[2] proposed this method for the analysis of sulfur dioxide contaminant in ambient air. The dynamic range quoted for this technique is suitable for use as a referee stack gas monitoring procedure; however, our experience leads to the conclusion that frequent standardization is necessary to obtain working curves (calibration curves are not linear). These conclusions are discussed in the following sections.

An in-house volumetric method using barium perchlorate with Sulfanazo III visual end point was modified according to work done by Dragusin and Gavriliuc[3] for analysis of sulfur dioxide for sampling by absorption scrubbers. The same range for sulfur dioxide determeination quoted for the thorin method is applicable here also.

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* This work was accomplished prior to the selection of the barium perchlorate-thorin or method 6, New Source Performance Standards, 23 December 1971.

EXPERIMENTAL

Experimental conditions, reagent concentrations, titration media, apparatus, procedures and calculations are presented very briefly for general information; details of methodology can be found in those papers referenced in the introduction.

Barium Perchlorate - Thorin Method [$Ba(ClO_4)_2$ = .01M]

a) Use 40 ml scrubber solution sample, run blank concurrently.
b) Add 4 times sample volume of 80% IPA.
c) 2-3 drops thorin (0.2% in H_2O).
d) Titrate with standard $Ba(ClO_4)_2$ from yellow to light pink. Blank: 40 mls of 3% H_2O_2 solution.
e) Calculations of ppm SO_2 by $Ba(ClO_4)_2$ titrations:

$$SO_2, \text{ ppm} = \frac{[\text{Net mls } Ba(ClO_4)_2 \times \text{M of } Ba(ClO_4)_2]\ (24.47 \text{ ml/mmole})\ (10^3)\ (\text{dilution factor})}{\text{liters of gas at standard conditions (25°C and 760 mm Hg)}}$$

$$\text{Dilution factor} = \frac{\text{total scrubber sample volume}}{\text{aliquot taken for test}}$$

Barium Perchlorate - Sulfanazo III Method [$Ba(ClO_4)_2$ = .01M]

a) Pipet 40 mls of sample to one flask. Pipet 40 mls of blank to another flask.
b) Add 40 mls of acetone to both
c) Add 3-5 drops Sulfanazo III to both
d) Titrate to light blue endpoint (blank preparation as Thorin procedure).
e) Calculations of ppm SO_2 by $Ba(ClO_4)_2$ titrations:

$$SO_2, \text{ ppm} = \frac{[\text{Net ml } Ba(ClO_4)_2 \times \text{M of } Ba(ClO_4)_2]\,(24.47 \text{ ml/mmole})(10^3)\ (\text{dilution factor})}{\text{liters of gas at standard conditions (25°C and 760 mm Hg)}}$$

Acid-Base Titration with Phenophthalein (NaOH = 0.02 M)

a) Use 30 mls scrubber solution sample (30 mls 3% H_2O_2 served as blank).
b) Add 5-10 drops phenophthalein indicator.
c) Titrate to first light pink color.
d) Calculation

$$SO_2, \text{ ppm} = \frac{\left[\frac{\text{millimoles NaOH}}{2}\right] \times (24.47 \text{ ml/mmole}) \times (10^3) \times (\text{dilution factor})}{\text{liters of gas at standard conditions (25°C and 760 mm Hg)}}$$

Barium Chloranilate Method

a) Standardization:

1. Weigh out 931.0 mg of sodium sulfate [45.1% as SO_4] and make up volume in a 1000 ml volumetric flask with deionized water. Concentration of solution, SO_2 per milliliter equals 45.1% x 931.0 mg/liter = 419.9 µg/ml.

$$\frac{419.9\ \mu g/ml}{64.06\ MW\ SO_2} \times 24.47\ \mu l/mole = 160.6\ \mu l/ml$$

2. Pipet 15 ml of solution No. 1 into a 100 ml volumetric flask and dilute with deionized water. This yields a solution containing, 24.09 µl of SO_2/ml.

3. Pipet 5 ml, 10 ml, 15 ml and 20 ml of above solution into separate 100 ml volumetric flask (don't dilute to mark). This yields solutions containing 1.2, 2.4, 3.6, 4.8 µl of SO_2/ml respectively.

4. Add to each of the above flasks and to an empty volumetric flask (blank) 10 ml of a KHP buffer and 50 ml of 95% ethanol.

5. Add dilute HCl to obtain pH 4.0 on final solution.

6. Add ~0.3 g of barium chloranilate and dilute to volume.

7. Shake for 10 minutes on auto shaker.

8. Filter through Whatman No. 40 paper or equivalent and run samples on DK-2A or similar spectrophotometric at 530 mµ versus a blank prepared in the same manner.

9. Operating Conditions for Beckman DK-2A

- Measure absorption at 530 mµ versus a blank in the reference cell.
- Tungsten lamp.
- Photomultiplier detector.
- 1 cm or 10 cm cells (depending on concentration).

b) Sample analysis:

Take suitable aliquot from scrubber sample solution and treat as above.

c) Calculation:

Read directly from standard curve, correcting for dilution and volume of gas.

Stack Sampling Apparatus

The apparatus for sampling stack gas was adapted from the standard thorin indicator method for use in the laboratory. Figure 1 shows the components of this absorber train. A standard certified 875 ppm SO_2/N_2 gas blend was substituted for the probe. The 875 ppm sulfur dioxide/nitrogen blend was drawn through the 50 ml of H_2O_2 scrubber solution into the calibrated evacuated volume while monitoring the pressure with a transducer. For this standard gas blend 3.6 l to 14.4 l volume samples were used. It was found that flows faster than 1.0 liter/minute could result in SO_2 loss therefore, the rate used here was 0.5 liters/minute through the modified ASTM lamp sulfur scrubbers.

The following formula was used to correct gas volume to standard conditions (25°C and 760 mm Hg).

$$V_s = V_t \left[\left(\frac{298}{T_f+273} \times \frac{P_f}{760} \right) - \left(\frac{298}{T_i+273} \times \frac{P_i}{760} \right) \right]$$

Where: V_s = vol. of gas sample at standard conditions in liters

V_t = vol. of calibration tank in liters

T_f = final temperature, °C

T_i = initial temperature, °C

P_f = final pressure, mm Hg

P_i = initial pressure, mm Hg

RESULTS AND DISCUSSION

Repeated standardization for the barium chloranilate method over a wide concentration range (0-400µg/ml sulfur dioxide) resulted in non-linear and non-reproducible curves. It was found that pH was even more critical than expected and careful adjustment to pH 4.0 with dilute HCl was necessary.

Because of these problems a working curve was prepared for the concentration range from 0-10µg of sulfur dioxide per ml (0.4µl/ml) resulting again in a non-linear curve at pH 4.0 (See Figure 2). Reproducibility of the curve from day to day was not good.

A Bausch & Lomb 340 Colorimeter and a Beckman Model DK2A Spectrophotometer were both evaluated for use with the barium chloranilate method. The B&L 340 was totally inadequate for this analysis.

Critical pH, necessity for filtering, mixing time, and the difficulty in reproducing the calibration curve makes the barium chloranilate method impractical for use in the field test program.

The following tables give results obtained from the volumetric procedure. Statistical evaluation of the data indicates that there is essentially no major difference in the precision of the thorin and Sulfanazo III methods. The mean values of the thorin and acid-base titrations are not significantly different from the certified value (875 ppm) but the mean value is significantly different for the Sulfanazo titration. This bias maybe related to selection of the point of color change.

COMPARISON OF VOLUMETRIC TECHNIQUES FOR SULFATE ANALYSIS

(PPM SO_2)

Volume of Sample (liters at STP*	Thorin	Sulfanazo III	Acid-Base (phenophthalein)
3.63	896	863	897
14.4	893	852	878
14.4	860	831	833
14.4	872	879	---

*Certified from vender as 875 ppm SO_2

	Thorin	Sulfanazo III	Acid-Base
Sigma value	17.2	20.2	32.9
Mean ($\bar{x}$)	880	856	869

The speed and simplicity of these methods suggests that one be used as the referee technique. Given the above data, the barium perchlorate-thorin method appears to be the preferred technique.

REFERENCES

1. Bertolacini, R. J., and Barney II, J.E. Anal. Chem., 29, 281, (1957)
2. Kanno, S., Int. J. Air Poll. 1, 231-33 (1959)
3. Dragusin, I. and Gavriliuc Angela, Revue Roumaine de Chimie, 12, 1239-43 (1967)

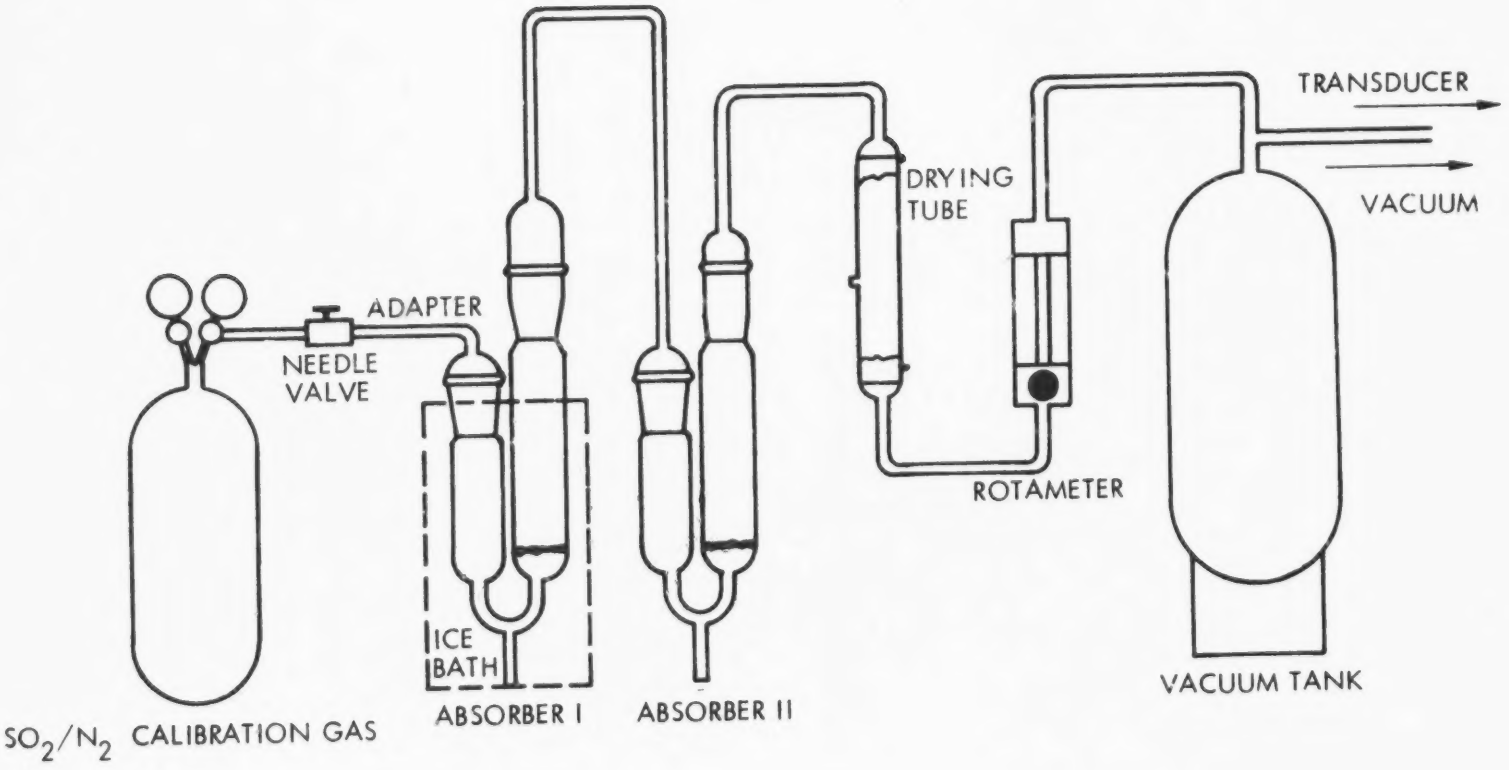

Figure 11-2 Apparatus for Sampling SO_2/N_2 Simulated Flue Gas

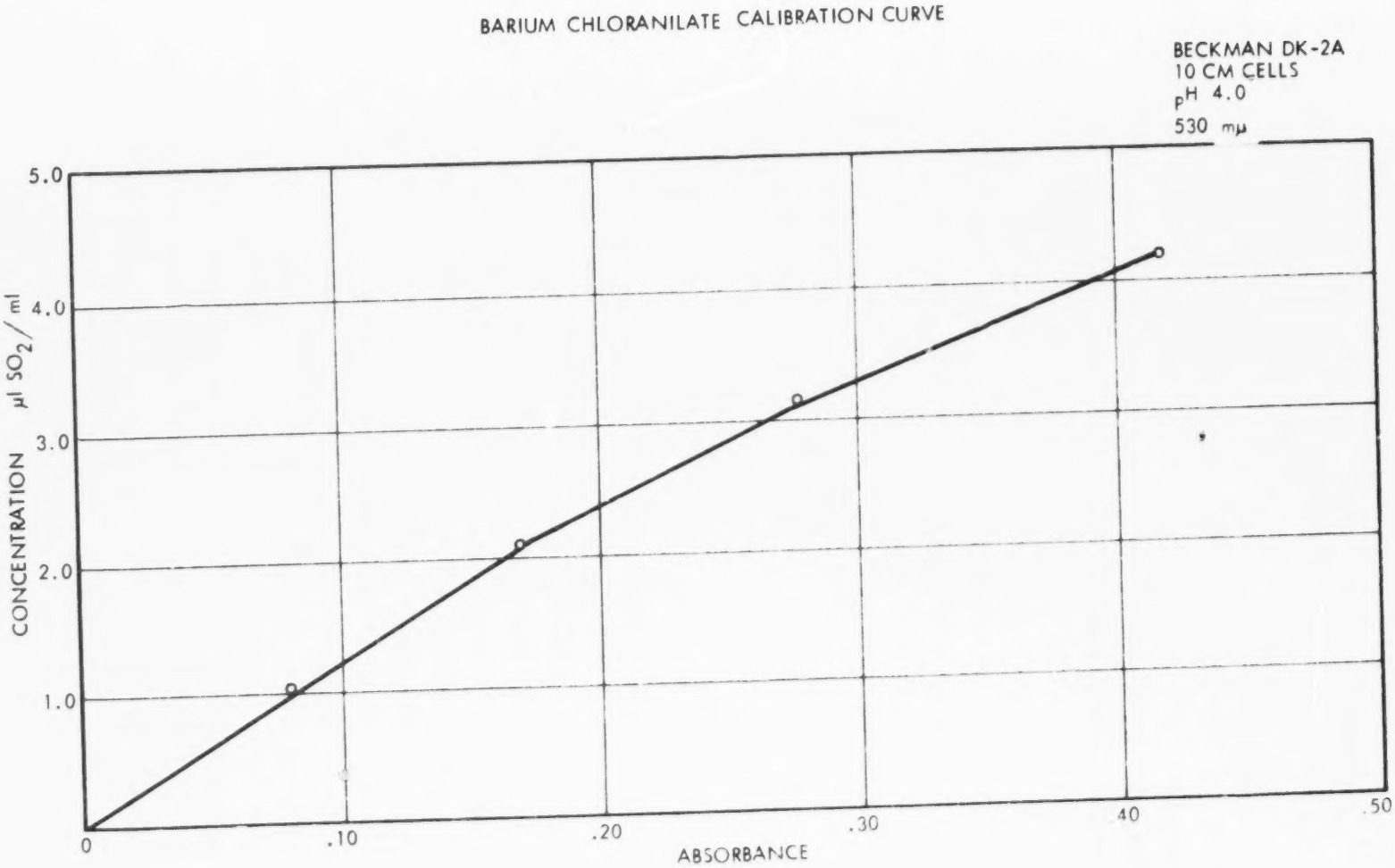

Figure 21-1 Barium Chloranilate Calibration Curve

TASK F

PROCUREMENT AND INSTALLATION OF SO_2 MONITORING EQIPMENT

The scheduled installation of power to the trailers by the Nevada Power Co. was delayed several times because of the more critical demand on their personnel to trouble shoot and maintain their power plants operating. In addition to the manpower delays, TRW had to purchase a transformer for use as the power company did not have adequate service to supply their power needs. Finally, 240 volt, single phase, 120 amp service was installed to both trailers. Transient noise and power fluctuations including 60 cycle ground loop noise, 60 and 120 cycle spiking noise were observed. These line problems were remedied as required by rewiring, use of Sola and isolation transformers and filters, but only to the extent that is reasonable for field installation. If an instrument was unduly susceptible to minor line noise or was generating noise itself, these observations were documented an an instrument deficiency.

Sampling System

The Intertech stack probe, designed for high particulate loading, (i.e., the unit that incorporates a shield on the in-line or in-stack filter), was tested in conjunction with the Intertech NDIR in the Unit 1 breaching duct. The probe and heat traced Teflon lines were equilibrated at 300°F prior to drawing the sample stream to the instrument. The probe became completely clogged (packed) with particulate matter in a relatively short duration ($\sim$ several hours). A back pressure of 30 psig gave no indication of backpurge flow. Only the partial shield was used (protecting the filter from direct impingement by the flue gas stream) and the effective filtration area of the filter may have been diminished in previous testing. When this unexpected failure occurred, it became quite apparent that the Project Officer's suggested approach, described as the contingency sampling plan in Task E, should be immediately implemented.

The details of the complete sampling system incorporating the flue gas stream diversion approach is shown in Figure F-1. The heat traced insulated sample line from the duct is 3" Aluminum Schedule 40 conduit pipe. Originally an order was placed for an American Air Filter Co. blower (5) with 2 h.p. motor and a 9K industrial exhauster for 300°F abrasion resistant service.

Since the manufacturer was unable to supply the unit as specified by the required delivery date, the order was cancelled in favor of the following blower purchased from Smallcomb Electric Co. with a 5-day delivery guarantee:

> Size 6, Type CI Clarage blower, Arrangement 9, THBW, 3845 RPM, complete with drive and variable pitch pulley on 220 VAC single phase 1-1/2 HP motor specifications: 340 CFM at 10" water static pressure.

The Clarage blower had 6" round inlet and discharge openings which required adaptation to the 3" sample line. The adapters were fabricated at the TRW Redondo Beach facility.

In order to ensure a homogeneous gas stream at the sample manifold the minimum pump capacity to give 37.5 ft/sec (=2250 ft/min) linear velocity or a sufficiently high Reynolds number (>30,000) through the 3" aluminum pipe was calculated. The CFM of 128 ft^3/min could be handled by a 0.25 h.p. motor.

Continuing downstream, to the sample manifold (⟨6⟩), a section of 3" IPS pipe 4 ft. long was modified to provide 10 outlets for either single instrument sampling or multiple-parallel filtering of sample gas for as many instruments as would be installed in the downstream instrument manifold. Outlets from the stack gas manifold were provided with a 3/4" straight pipe thread required to fit the Intertech filter housing thereby allowing primary filtering at that point. Fabrication of the manifold has been completed. This design of parallel filtering through 10 filters that were designed for in-stack operation was a fail-safe system from the standpoint of particulate clogging. It gave long term continuous flow through service

with a minimum of back purge required.

As a precaution, however, a second type of filter unit purchased from AMF Cuno Division of AMF was procured for evaluation in the event expanding the number of parallel filters becomes necessary. The description of this filter equipment is as follows:

Type 1B1 Filter Housing (cast iron)

Microscreen cartridge 200 mesh (~75 microns)

Porolkean cartridge 20 micron

Mircorscreen cartridge 2 micron

Teh cartridges are constructed of stainless steel and are cleanable by ultrasonic methods for reusability. Viton gaskets were specified for high temperature service. Use of these filters was not required as the primary design using Intertech filters operated in a satisfactory manner during the test period.

Flue Gas Velocity Mapping and Installation of Trailer

The flue gas in the upper half of the duct work of Unit 1 was mapped vertically downward from each of the four access sampling ports to determine relative flow velocities and respective flow directions. The probe was that shown in Figure E-1. It was found that on a continuous downward traverse, all flow directions were parallel to the main mass flow in the duct and the area of msximum velocity was approximately four feet below sample ports B and C (Figure F-2) at the mid-line of 11 feet. The relative velocity was 1/2 of the maximum. The temperature of the flue gas was 108°C (240°F). The velocities were not calculated as this information was not relevant because the unit was operating at 75% of the full power rating due to a missing water preheater.

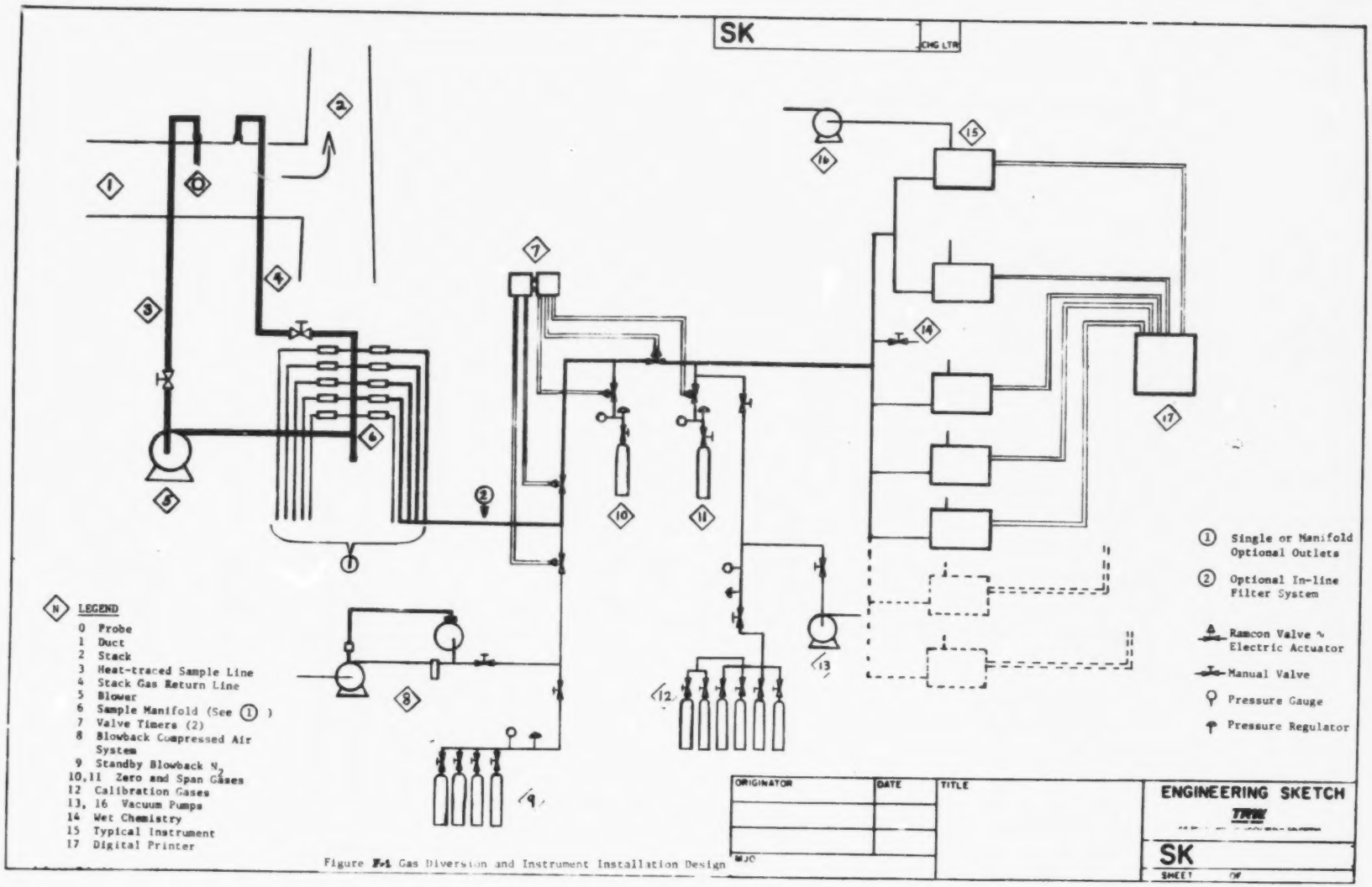

Figure 5-1 Gas Diversion and Instrument Installation Design

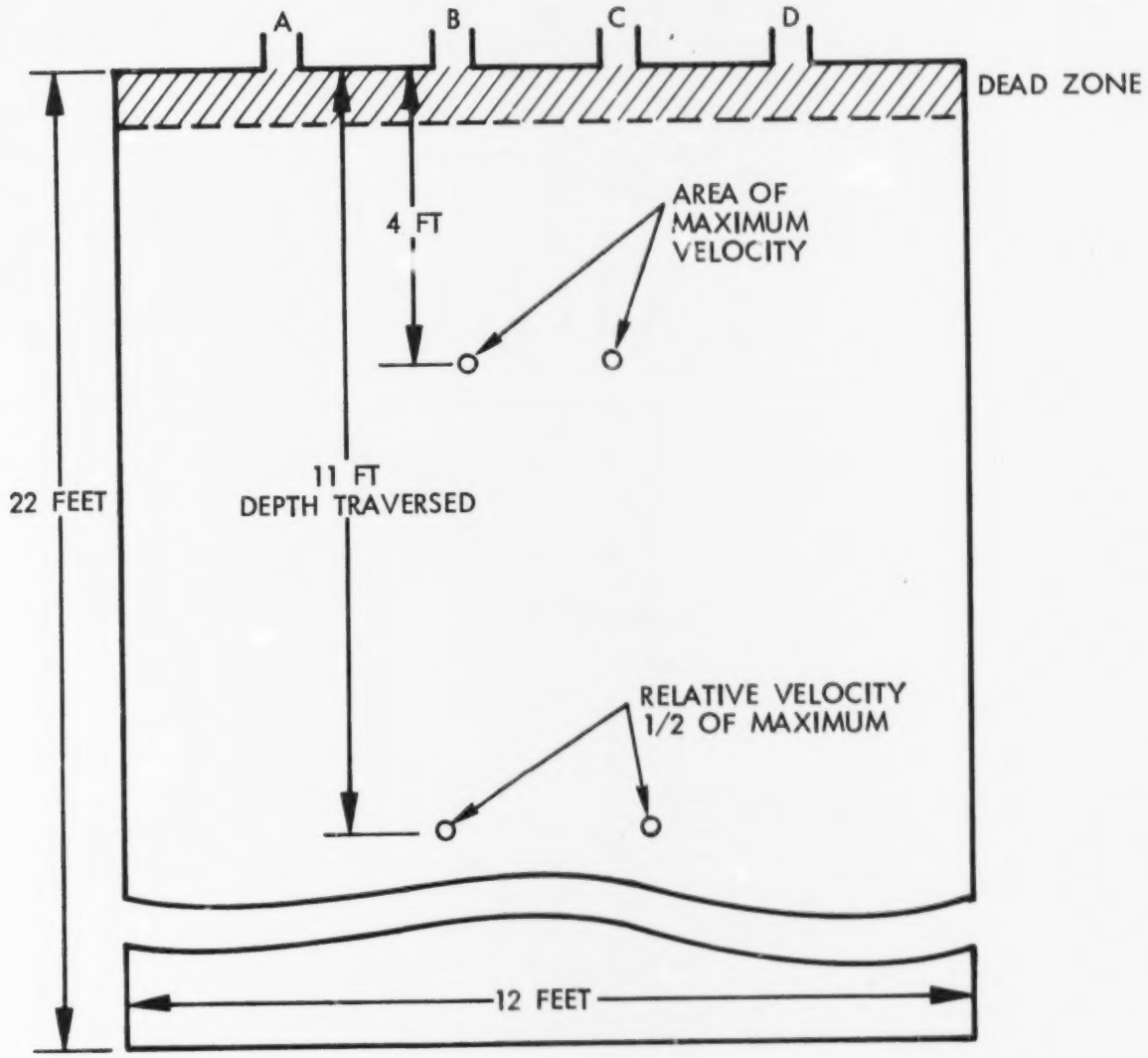

FIGURE F-2 RELATIVE VELOCITY PROFILE OF UNIT 1

TASK G

Field Test Program

The field test program was started on the 10th of May, 1971 when the nominal installation of all the monitors was accomplished by TRW personnel. The Bendix UNOR-6 monitor was delivered and installed in mid June. The remaining time in May was spent in the usual sort of trial operation and error debugging, of which the following is typical.

After one week of continuous operation, on 21 May 1971, unusually low SO_2 values on the order of 90 ppm were noted on the instruments along with abnormally high oxygen and low carbon dioxide values, approximately 15% and 7.5%, respectively. Shortly after this was noted a heat trace line short caused melting of two Kynar tees. These tees are temperature rated well within the normal operating temperature for our system (300°F upper limit for continuous use as compared to 200°F for the sample transfer line). Subsequently, the entire system was refurbished with new fittings, heat tracing and insulation. The short problem was identified as a specific friction/pressure contact at the base of the 10 port manifold which was corrected in the rewrap.

The relatively routine operation began about the first of June 1971. The Esterline-Angus data recording system (model D-2020) was set to record values from each instrument at hourly intervals. TRW recorded 10 points at 6 second intervals each hour, the data tables show the mean value of the 10 millivolt readings and the standard deviation. In this manner, one could evaluate short term noise, voltage spikes, etc. A very stable instrument whould show a very small standard deviation of the readings. In the case where manual wet chemical samples were taken, the printer recorded 10 readings from each instrument over the 10 minute sampling period for

the wet method. In this manner, the mean values for instruments and wet analyses should be directly comparable. The sample line back-purge, zero and span gas valves and data system were connected to a series of timers which permitted semi-automated operation.

The data acquisition phase ran from 1 June 1971 to 31 August 1971 with periodic interruptions due to operating failures in the power plant boiler. The plant was down from 12 July to 24 July 1971. The sampling, filtering, calibration and sample delivery system operated exceptionally well throughout the entire test period requiring only minor maintenance. (Tighten fittings, oil pump motors.) Table G-1 contains a brief abstract of the maintainance log during the field test period.

Figures G-1 thru G-6 show the individual analyzers and sample conditioning equipment for each unit as they were installed during the test program. All analyzers and sampling equipment were fed with a common 1/2" heated line containing the stack effluent gas at stack conditions of temperature, CO_2 and water content, but filtered to remove particulate matter. Each analyzer was equipped with whatever sample conditioning was suggested in the instruction manuals. Table G-1 contains an abstract of the maintainance log kept by TRW.

It should be noted here that the wet chemical analysis did not agree with the vendor's "certificate of analysis" provided with the bottle. This seems to be a common problem which has been noted by EPA equipment users and research facilities for some time! Calibration gas vendors are apparently capable of blending gases to within quite reasonable tolerances $\pm$ 5 to 10% at the 200 ppm level, but are unable to provide a good certified analysis of exactly what is present. Table G-2 illustrates this problem.

Table G-3 contains the typical millivolt readings from the instruments. The channel assignments were:

Channel 1 - Calibrated Instruments MSK-SO_2-E_1

Channel 2 - DuPont 460

Channel 3 - Intertech URAS-2

Channel 6 - Dynasciences SS330/CS1000

Channel 7 - ITT Barton 400

Channel 8 - Bendix UNOR-6

The notes and "true value" columns contain annotations as to function being performed (span-gas, zero gas, calibration gas), and the "true value" as indicated by the wet chemical analysis of the stack gas at that time or the wet chemical analysis of the span or calibration gas bottle in use at that time.

Rather than burden the report with the mass of hour by hour routine data obtained over the three months of testing, Table G-3 illustrates typical data obtained during the period. The actual data used in each analysis phase will be detailed in concise tables under Task H, Data Reduction.

TABLE G-1

ABSTRACT OF MAINTAINANCE LOG

DuPont SO_2 Analyzer - Instrument was fully operational before June. Malfunction problems were encountered in mid June were related to modifications made during field installation. Output range was changed from 5 millivolts to 10 millivolts by factory service representatives in late June.

Intertech URAS-2 SO_2 Analyzer - Instrument made operational by TRW before June. 22 June 1971 defective tubes in amplifier replaced. This maintenance item for the URAS-2 NDIR has been included as part of the installation discussion because the EPA owned unit was previously used on another program and the unit not refurbished prior to the current test. No other operational problems were encountered.

Calibrated Instruments - Instrument installed by TRW in May. 16 June factory representative checked instrument and made recommendations.

Bendix UNOR-2(NDIR) - Received 2 June and installed by TRW on June 8. June 22 factory representative placed instrument in operation. June 28 analysis of data revealed that Bendix not operational. Repaired 14 July 1971 by factory service personnel.

Dynasciences SO_2 Analyzer - Non-operative June 2 needed cooling for water knockout. 7 June TRW supplied cooling system installed.

ITT Barton - 7 June instrument rendered operational by TRW personnel. No valid operating data obtained for June because of extremely slow response time, etc. Although several calls were placed to vendor to assist and evaluate in the field installation, no positive response was obtained.

TABLE G-2

CALIBRATION GAS ANALYSIS (ppm SO_2)

Requested Level	Vendor certified Level	Wet chemical Analysis Level(a)	Number of Analyses
		mean ± S.D.	
200	205	216 ± 2.4	12
400	400	413 ± 3.3	9
600	660	646 ± 7.6	12
900	824	812 ± 3.2	12
1000	1080	1036 ± 4.2	12
900	880	859 ± 3.2	3

a. The analytical technique used is discussed in appendix E-1.

TABLE G-3

Typical **Routine Data**

M.V. Means and Standard Deviations as a Function of Time

Julian Date	Time	Channel 1	2	3	6	7	8	True Value
161	10:11	95.53	3.295	8.331		57.29		ppm SO_2
		.419	.0425	.0120		.191		
162	9:00[b]	29.62	1.216	3.252		33.52		229±2
		.383	.150	.056		.597		
Zero	10:05	1.92	.134	.198		4.77		
		.0919	.051	.0187		.116		
162	10:45	27.62	1.20	3.02		35.7		
		.563	.1077	.0778		.259		
Zero[b]	10:52	1.966	.0267	.133		6.17		
		.058	.0012	.0115		1.17		
Span[c]	10:57	94.6	3.55	8.64		55.6		871
		.777	.156	.051		1.06		
Zero	11:03	1.87	.007	.263		9.1		
		.115	.093	.032		1.01		
162	11:09	22.7	1.14	2.896		35.4		
		2.65	.065	.0776		1.432		
Span	11:40	98.02	3.286	8.63		58.04		871
		1.7	.559	.132		1.124		
162		0	1.362	2.924		35.9		280±3.3
	12:08[b]	0	.104	.0483		.187		
162	12:16	93.0	3.984	8.62		57.22		871
Span		.354	.1374	.0055		.3033		
162	12:20	4.44	.162	.262		162		
Zero		.445	.025	.030		.856		
165	12:23	23.86	.032	2.48		31.46		
		.219	.058	.011		.0548		
Span	17:15	0	3.336	8.67		62.62		871
		0	.0396	.0141		1.931		

Table G-3 (Continued)

Julian Date	Time	Channel 1	2	3	6	7	8	True Value ppm SO_2
166	9:00	.22 .0224	2.868 .00837			34.18 .0837		
166	11:04		.334 .0344	2.71 .007		32.78 .1643		
166	12:00		.19 .042	2.71 .03		47.74 1.014		
166	14:00	- -	.084 .032	2.876 .006		32.3 .141		
166	16:00	25.98 .164	.074 .0643	3.072 .413		29.86 .134		
Zero	17:19	1.8 .1	.794 .12	.10 .01		3.42 .13		
Span	17:25	89.38 .606	3.02 .08	8.47 .02		52.9 .33		871
166	17:30	27.4 .19	.448 .05	3.07 .035		33.82 .11		
167	8:34	25.8 .27	.99 .05	2.81 .01		3.04 .15		
167	11:00	25.3 .1	1.32 .05	2.61 .01		29.04 .1		
167	15:01	26.2 .2	1.16 .1	2.65 .03		16.9 1.6		
167	16:06	25.8 .2	1.08 .08	2.63 .02		21.0 .07		
168	10:05	23.5 .1	.952 .02	2.54 .01		23.7 .02		
Zero	10:13	1.76 .05	0 .03	.66 .05		4.18 .32		
Span	10:18	90.84 .89	4.05 .06	8.73 .04		39.64 .45		871
168	13:00	24.0 0	1.25 .04	2.46 .01		24.2 .1		

Table G-3 (Continued)

Julian Date	Time	Channel 1	2	3	6	7	8	True Value
172	11:18		1.14 .06	2.59 .01		24.4 .1		ppm SO_2
172	13:00		1.02 .05	2.82 .01		0 0		
172	14:14	25.1 .1	.87 .09	2.94 .01		23.78 .09		
172	15:00	25.7 .2	.33 .03	3.03 .01		23.5 .2		
173	8:43	24.2 .2	.102 .04	.12 .03		25.3 .09		
173	11:11[b]	25.4 .2	1.21 .04	.248 .025		27.62 .08		262±8.6
179	15:00	29.84 .167	.77 .0583	2.936 .0089	1.15 .02	25.44 .114		
179	17:00	30.46 .089	.824 .0456	3.124 .0114	1.72 .02	25.42 .277		
179	19:00	30.22 .217	.956 .0477	3.072 .0082	1.66 .01	25.6 .100		
180	9:00	28.82 .228	.878 .0327	2.74 .0071	.92 .02	27.42 .1095		
Zero	9:50 .0837	1.78 .0853	.212 .0466	.172 .02	.02 .122	4.4		
Span	10:05	92.86 .513	3.4 .056	8.21 .0783	2.76 .17	50.56 1.49		871
180	11:01	30.0	.964	2.848	1.12	29.46		
180	13:01	30.66 .048	1.022 .055	2.936 .0055	1.19 .02	27.36 .0894		
180	15:00[b]	31.34 .152	.982 .0795	3.04 .0122	1.11 .02	27.08 .130		288±6
Zero		1.94 .0894	.0417 .0337	.054 .0688	.22 .04	3.70 .158		

Table G-3 (Continued)

Julian Date	Time	1	2	3	6	7	8	True Value ppm SO_2
Span	15:19	94.52 .432	3.448 .0492	8.456 .0365	3.57 .21	57.88 2.21		871
180	17:00 [b]	32.12 .259	.954 .0573	3.178 .053	.17 .01	27.5 .300		278±4.0
181	9:00	30.68 .295	.13 .0506	2.784 .0152	.77 .02	27.3 .1225		
181	31.2	.984 .1414	2.866 .0397	1.70 .0089	26.2 .03	.100		
181	13:00	30.8 .173	.850 .0469	2.88 .0173	1.66 .04	25.38 .130		
181	15:00	31.3 .235	.944 .023	2.92 .0141	1.64 .02	25.44 .0894		
182	9:00	31.42 .148	.914 .0602	2.776 .0055	2.08 .02	24.88 .0837		
182	13:00	31.22 .164	.986 .077	2.736 .0089	.31 .03	26.0 .100		
182	15:00	.396	.0482	.0114	.02	.100		

[a]Channel Identification:

1. Calibrated Instruments
2. DuPont
3. Intertech
6. Dynasciences
7. ITT Barton
8. Bendix

[b]Simultaneous sample - Analysis by barium perchlorate - thorin titration

DATA SUMMARY

	TIME	CHANNELS 1	2	3	6	7	8
DATE 182							
			ZERO				
MV	10.31	0.00	-1.96	-.23	-.84	3.10	.61
MV	10.31	0.00	-.19	-.22	-.72	3.10	1.56
MV	10.31	0.00	-.10	-.23	-1.40	3.00	1.61
MV	10.31	0.00	-.19	-.22	-1.01	3.10	.41
MV	10.31	0.00	-.13	-.26	-.93	3.10	1.35
			CALIBRATION	660 PPM			
MV	10.45	78.60	2.47	6.12	.81	47.80	1.51
MV	10.45	78.90	2.48	6.11	.46	47.50	1.29
MV	10.45	78.80	2.51	6.11	.57	47.40	.52
MV	10.45	78.30	2.52	6.13	.71	47.60	.68
MV	10.45	78.60	2.56	6.10	.72	48.10	1.31
			CALIBRATION	190 PPM			
MV	11.00	25.80	.71	1.42	.41	30.70	.53
MV	11.00	25.90	.81	1.42	.40	30.50	1.68
MV	11.00	26.10	.76	1.43	.45	30.50	1.49
MV	11.00	25.80	.76	1.42	.41	30.40	1.09
MV	11.00	25.80	.77	1.41	.41	30.40	.63
			CALIBRATION	1080 PPM			
MV	11.14	98.80	4.25	9.77	1.53	51.10	2.47
MV	11.14	98.90	4.19	9.79	1.58	51.10	2.73
MV	11.14	98.30	4.17	9.78	1.58	51.10	2.49
MV	11.14	98.80	4.27	9.78	1.65	51.10	2.78
MV	11.14	99.10	4.30	9.79	1.66	51.30	2.54
			CALIBRATION	400 PPM			
MV	11.30	49.40	1.65	3.41	1.08	47.60	1.89
MV	11.30	49.60	1.64	3.42	1.07	47.40	2.35
MV	11.30	49.60	1.65	3.40	1.09	47.70	2.59
MV	11.30	49.50	1.65	3.40	1.08	47.90	1.46
MV	11.30	49.30	1.63	3.41	1.04	48.30	1.63

TABLE G-4

TYPICAL CALIBRATION DATA

TABLE G-4 (Continued)

			CALIBRATION	880 PPM			
MV	11.42	99.00	3.51	8.03	1.57	54.90	3.92
MV	11.42	99.10	3.50	8.01	1.57	54.80	3.91
MV	11.42	99.00	3.56	8.00	1.62	54.90	2.70
MV	11.42	99.20	3.50	8.02	1.62	55.20	2.74
MV	11.42	99.30	3.57	8.04	1.58	55.30	3.48

STATISTICS SUMMARY

TIME	CHANNELS 1	2	3	6	7	8
DATE 182						
			ZERO			
ACTUAL						
MV MEANS	0.00	-.	-.23	-.98	3.08	1.11
MV SIGMAS	0.000	.809	.016	.258	.045	.559
			CALIBRATION 660 PPM			
ACTUAL						
MV MEANS	78.64	2.51	6.11	.67	47.68	1.06
MV SIGMAS	.230	.036	.011	.130	.277	.434
CORRECTED						
MV MEANS	78.64		6.35	1.65	44.60	-.05
MV SIGMAS	.230		.020	.289	.281	.708
			CALIBRATION 190 PPM			
ACTUAL						
MV MEANS	25.88	.76	1.42	.42	30.50	1.08
MV SIGMAS	.130	.036	.007	.019	.122	.508
CORRECTED						
MV MEANS	25.88		1.65	1.41	27.42	-.02
MV SIGMAS	.130		.016	.259	.130	.756
			CALIBRATION 1080 PPM			
ACTUAL						
MV MEANS	98.78	4.24	9.78	1.62	51.14	2.60
MV SIGMAS	.295	.055	.008	.034	.089	.143

TABLE G-4 (Continued)

CORRECTED						
MV MEANS	98.78		10.01	2.60	48.06	1.49
MV SIGMAS	.295		.018	.261	.100	.577
		CALIBRATION	400 PPM			
ACTUAL						
MV MEANS	49.48	1.64	3.41	1.07	47.78	1.98
MV SIGMAS	.130	.009	.008	.019	.342	.477
CORRECTED						
MV MEANS	49.48		3.64	2.05	44.70	.88
MV SIGMAS	.130		.018	.259	.345	.735
		CALIBRATION	880 PPM			
ACTUAL						
MV MEANS	99.12	3.53	8.02	1.59	55.02	3.35
MV SIGMAS	.130	.034	.016	.026	.217	.602
CORRECTED						
MV MEANS	99.12		8.25	2.57	51.94	2.24
MV SIGMAS	.130		.023	.250	.221	.822

TABLE G-4 (Continued)

CALIBRATION CURVES

MV READINGS

GAS CONC	CHANNEL 1	2	3	6	7	8
660						
MEAN	71.95	3.12	6.15	2.08	43.73	.94
LOWER	57.01	2.97	5.92	1.50	33.10	-.72
UPPER	86.89	3.27	6.38	2.65	54.36	2.60
190						
MEAN	30.98	1.28	1.71	1.48	33.62	.04
LOWER	15.48	1.13	1.47	.88	22.59	-1.69
UPPER	46.49	1.44	1.95	2.07	44.66	1.76
1080						
MEAN	108.56	4.76	10.12	2.62	52.76	1.75
LOWER	93.09	4.61	9.88	2.02	41.76	.03
UPPER	124.03	4.91	10.36	3.21	63.77	3.47
400						
MEAN	49.29	2.10	3.69	1.75	38.14	.44
LOWER	34.18	1.96	3.46	1.16	27.39	-1.24
UPPER	64.39	2.25	3.93	2.33	48.89	2.12
880						
MEAN	91.12	3.98	8.23	2.36	48.46	1.37
LOWER	76.03	3.83	7.99	1.78	37.72	-.31
UPPER	106.22	4.13	8.47	2.94	59.21	3.05

TABLE G-4 (Continued)

TASK H

Data Evaluation

The field test program ended on 31 August 1971 after approximately 90 days of on-line testing were completed. Tables G-3 and G-4 show typical "field" and "calibration" data obtained during the period. For simplicity and ease of reference, the data actually used for the analysis programs are reproduced in the appropriate tables when a particular analysis is discussed.

Table H-1 contains the data used in computing the accuracy of the units under test. The reference value given in column 2 is the value of SO_2 concentration in ppm (wet basis) given by triplicate reference method analyses of duplicate samples taken from the sampling manifold (Fig. F-1, point 14) at the same time the instrument readings were taken. The indicated instrument values were the mean values of 10 readings taken at 1 minute intervals during the 10 minute wet chemical sampling period. The reference method used was described in Appendix E-1. The values indicated for Channel 3 were corrected for water vapor.

Table H-2 shows the analysis of the monitor's accuracy using the data in Table H-1. Calculated were the average error, $\bar{E}$, in ppm, the variance around $\bar{E}$, the standard deviation, and the 95% confidence interval according to the following:

(1) mean $\quad \bar{E} = \frac{1}{N} \sum_{1}^{N} E_i$

(2) variance $(s^2) = \dfrac{n\left(\sum_{1}^{N} E_i\right)^2 - \left(\Sigma E_i^{\,2}\right)}{n(n-1)}$

(3) standard deviation $= \sqrt{s^2} = \sqrt{\text{variance}}$

(4) confidence interval $\quad CI(95\%) = \bar{E} \pm t\left(\dfrac{s}{\sqrt{n}}\right)$

where

n = number of observations

s_i = value of an individual observation

t = percentile of the t distribution for $t(1-\alpha/2)$ and df = n-1

From Table A-4, Handbook 91, Experimental Statistics, National Bureau of Standards, 1963, $\alpha = .05$

The data produced by instruments connected to Channels 6 and 7 of the data system were completely anomalous at the times at which wet chemical samples were taken. Therefore, we are unable to indicate paired data points for these channels.

Table H-3 contains the data used to compute "calibration drift." There are two types of data analysis which can be used on the data in Table H-3. A linear regression vs time should show the effect of any systematic long term degradation effects as it does for Channels 1, 6 and 8. In the case of the instrument on Channel 8, the change in slope probably corresponded to the degradation of the sample cell. The same effect was noted in a similar program studying NO_x monitoring equipment.(a)

In the cases where no linear correlation can be established, the data is treated as normally distributed data around a central mean and the usual standard deviation, variance and confidence intervals are computed. Eimutis, in the NO_x monitor evaluation program, showed that the distribution is not truly normal but the error associated with this assumption are not large. The methods used are the same as for accuracy on Tables H-1 and H-2. The "calibration drift" analysis results are shown in Table H-4.

Table H-6 shows the results of a simple correlation of the millivolt readings for the various channels with each other and with the reference value. The data used was taken on days 214, 215, 216 and comprises 18 data sets including five reference tests and 1 each zero and span set. It should be noted that the monitors correlate far better among themselves (.9 or better) than with the reference method. Similar performance was

a. Instrumentation for the Determination of Nitrogen Oxides Content of Stationary Source Emission, Vol. II, APTD 0942, NTIS PB 209190, Monsanto Research Corporation, February 1972.

was noted in the NO_x monitor evaluation program conducted by Monsanto Research Corporation. A tentative explanation may be that despite our taking 10 readings per channel at one minute intervals that the average of these readings stlll does not adequately represent the 10 minute integrated sample taken in the reference method even though the overall accuracy obtained by comparing mean values is reasonably good. The low correlation of channel 8 with the reference value may be in part ascribed to a shifting zero point of the instrument during this period. The millivolt readings obtained during this time actually were smaller than the "zero" reading obtained prior to the reference tests.

Table H-7 contains data which illustrates that which we choose to call short term stability or rather short term "instability." The data are not the same as reproduceability, as these are consecutive millivolt readings for each monitor at about 10 second intervals with no change in pollutant level. Hence the difference from reproducibility. Reproduceability is the band around the mean values of successive measurements of the same level generally with some change in level intervening. Here we have a steady level and continuous readings which we record at 10 second intervals. Therefore we call this measurement "stability." Since these measurements were made using calibration gases of known steady composition there should be no source variations to consider here. Thus we can assign all the deviation in the readings to the stability or lack of stability in the basic instrument desgin.

The four tests already described constitute the major aim of our work. These are however, several factors which are of lesser importance but we have the data to investigate them.

In a laboratory when using a similar monitoring system for R and D work it is not unusual to calibrate the instrument at several points over the span. In the field, a user is more likely to put one calibration gas into the system near full scale and twist the span knob until he gets the same number. The obvious question is what type of error is introduced by this latter practice? To attempt to answer the question we treated the calibration data from one day in two ways as shown in Table H-9. We computed a calibration curve slope based on the millivolt readings

produced by a 1036 ppm calibration gas and used this value as a single point calibration. We then computed a least squares regression line based on all five calibration gas values and used this curve to predict a value for each mv reading to compare with the value given by the single point calibration curve. As can be seen from the final error figures in Table H-10, in some cases a single point calibration can lead to substantial errors in measurement. The instrument connected to channel 1 as a good case in point, having a departure from linearity above about 90% of span. After recomputing the linear regression calibration to exclude the 1036 ppm point the values changed from 10.00 ppm/mv slope and -70.2 ppm intercept to 8.66 ppm/mv slope and -14.8 ppm intercept. The error from the four point calibration curve fell from 2.9% of span to /02% of span or .2ppm. A similar single point calibration based on the 859 ppm calibration gas changed the slope from 10.48 ppm/mv to 8.66 ppm/mv which will change the single point calibration curve from 18% of span to less than 2% of span. The next logical question is what has been proved by this exercise. We consider that the following items have been illustrated:

a. The linearity of most properly operating equipment is within ±2% over most of their operating range.
b. The major departures from linearity occur at the extremes of the range (below 10% and above 90% of span).
c. If an instrument is known to be functioning correctly a single point calibration may be sufficient.
d. When an instrument is not known to be functioning correctly or is functioning incorrectly, a single point calibration can lead to extremely large errors.

TABLE H-1

ACCURACY DATA VS REFERENCE METHOD (a)

DAY	REFERENCE VALUE	DATA CHANNEL 1	2	3(b)	6	7	8(c)
162	280	-	326.3	269.8			
173	262	231.2	260.2	234.2			
180	288	273.6	227.0	300.9	231.4		
180	278	281.4	219.0	315.4			
190	227	-	214.4	254.2			
216	289	219.8	239.3	268.0			254
216	241	214.8	231.3	266.4			204
216	241	219.8	221.1	264.8			207
216	331	227.8	232.5	273.8			204
216	284	225.8	215.5	273.8			314
224	245	238.8	253.4	274.4			86.8(d)
224	240	238.8	246.6	274.4			96.2(d)
230	183	-	237.5	-			30.5(d)
230	213	191.3	240.9	-			38.65(d)

a. all data ppm SO_2

b. output corrected for 4% H_2O content of stack effluent

c. unit placed in service day 215 after repair

d. shown for illustration, not used in error analyses

TABLE H-2

ACCURACY ANALYSIS [a]

	CHANNEL			
	1	2	3	8
Average error, E_a	- 31.7	-16.9	+5.3	-40.6
Variance s^2	959.5	1908	826	2507
Standard deviation	30.97	43.68	28.74	50.07
Number of samples	11	14	12	5
t. 975	2.228	2.160	2.201	2.776
Confidence interval (95%)	±20.80	25.21	18.26	62.16
$E/span_{(b)}$	-3.2%	-1.7%	-.5%	-4.1%
$95\%CI/span_{(b)}$	±2.1%	±2.5%	±1.8%	±6.2%

a. values are ppm SO_2

b. span set at 1000 ppm SO_2

TABLE H-3

CALIBRATION DRIFT DATA

JULIAN DATE	ELAPSED TIME	Channel 1		Channel 2		Channel 3		Channel 8	
		I (a)	S (b)	I	S	I	S	I	S
148	0	-	-	34.0	219.62	58.2	92.72	-	-
160	12	-	-	59.1	221.65	87.7	91.34	-	-
182	34	-16.2	8.67	-1.2	-236.29 (c)	49.9	97.67		(d)
196	48	24.1	10.50	-23.0	103.37	37.6	92.18	-	-
215	67	14.0	10.69	12.9	115.66	43.5	90.90	129.4	173.58
223	75	18.7	11.08	-19.9	106.60	-	-	149.3	165.85
231	83	9.5	11.12	10.4	97.85	3.4	87.69	151.29	165.03
236	88	16.5	10.47	-20.9	121.94	-15.4	88.00	140.0	159.5
238	90	18.1	10.67	97.1	128.13	3.6	90.84	138.6	161.0
239	91	17.4	10.72	24.3	129,57	36.9	79.15	133.5	158.96
243	95	-	-	31.9	130.13	-22.5	84.94	173.8	152.94

(a) I = Intercept of PPM vs MV curve for 5 calibration gases (ppm)

(b) S = Slope of PPM vs MV curve for 5 calibration gases (ppm/mv)

(c) output span voltage changed from 5MV to 10MV Fullscale

(d) Data for this date completely anamolous, no curve fit possible

TABLE H-3 (Continued)

DAY	ELAPSED TIME	Channel 6		Channel 7	
		I	S	I	S
148	0	3.7	139.38	-	-
160	12	-	-	260.0	8.46
182	34	-839.1	716.61	-726.0	29.87
196	48	-	-	-4081.9	110.92
215	67			-861.8	34.70
223	75			-	-
231	83			-139.1	18.42
236	88			38.8	28.54
238	90	-4.0	156.29	-23.2	17.8
239	91	-11.4	162.03	-2.4	23.34
243	95	7.0	165.25	-2.5	26.12

TABLE H-4

CALIBRATION DRIFT ANALYSIS

	CHANNEL						
	1	2	3	6	7	8	
Linear Regression analysis of slope data (Table H-3)							
Correlation coefficient	.895	.663	.657	.87	(a)	.877	
Slope (PPM/MV)/day	.045	.537	-.093	1.55	-	-.599	
Span Voltage	100MV	10MV	10MV	6.5MV	-	6.5MV	
95% Confidence interval about slope	.103	-	-		-	-1.4	(ppm/mv)
"Correlation with time" (b)	linear	random	random	linear	-	linear	
Analysis of non-time correlated channels							
Mean, x (ppm)	-	115.5	89.54	-	-	-	
Variance	-	111.32	22.49	-	-	-	
Standard deviation (ppm)	-	10.55	4.74	-	-	-	
Number of samples	-	11	10	-	-	-	
t. 975	-	2.228	2.262	-	-	-	
Confidence interval (95%)	-	7.08	3.4	-	-	-	
"Calibration drift" %span/24 hr	1.03%	.7%	.3%	1%	-	.9%	

a. anomalous data

b. linear means simple correlation coefficient of 0.9 or greater.

TABLE H-5

LONG TERM ZERO DRIFT

Date	Time	Ch 1	Ch 2	Ch 3	Ch 6	Ch 7	Ch 8
162	100.5	1.92	.134	.198		4.77	
162	1052	1.966	.0267	.133		6.17	
	1103	1.87	.007	.263		9.1	
	1220	4.44	.162	.262		162	
166	1719	1.8	.794	.10		3.42	
168	10:13	1.76	0	.66		4.18	
180	9:50	1.78	.212	.172	.02	4.4	
180	1510	1.94	.0417	.054	.22	3.70	
189	1748	1.94	.002	.106	-.084	2.88	
194	1347	-	.08	-.04	-	.54	-.82
194	1515	1.48	-.004	0	-	.57	-.81
195	10:11	1.94	.03	.07	-	.01	-.95
215	1539	1.86	.16	-.26	-	8.26	-1.21
218	0806	0.4	.18	-0.27	-	1.7	1.01
218	1147	0.58	.08	.54	-	1.1	1.04
222	1923	1.7	.27	.99	-	-	-
223	1633	1.9	-.004	-.26	-	1.20	1.02
224	1635	1.9	-.06	-.27	-	-	1.06
225	0953	1.7	-.15	1.18	-	-	1.01
228	1352	1.8	-.01	-	-	-	.96
228	1412	1.8	.08	-	-	-	1.08
228	1555	1.8	-.04	-	-	-	.77
229	0852	-	.08				.94
229	1558	.7	-.23				1.04

TABLE H-5 (Continued)

Date	Time	Ch 1	Ch 2	Ch 3	Ch 6	Ch 7	Ch 8	
230	1121	-	-.06	-.11			1.09	
230	1448	2.0	-.11	.20			1.19	
235	1500	0.42	.3	-.10				
235	2055	1.9	.25	.27				
237	1038	0	-.11	0		.6	1.01	
237	1508	1.8	.05	-.27		.24	1.01	
243	1339	0	.34	.22	-.09	.8		
243	1410	2.0	.16	-.24	-.08	.82		
mean zero point		1.62mv	.08	.12	-.003	2.86	.58	mv
variance		.67	.03	.13	.014	7.06	.68	
standard deviation		.82	.18	.36	.12	2.65	.82	mv
95% confidence interval		1.76mv	.36	.74	.33	5.6	1.73	mv
number of points		29	32	28	5	19	18	
calibration slope ppm/mv		11	120	90	160	28	160	ppm/mv
zero offset		1.8	.96	1.1	-.04	8.	9.2	% of span
zero band		1.9	4.3	6.7	5.3	15.7	27.7	% of span

a. Time is 24 hour clock

TABLE H-6

MONITOR CORRELATIONS

Data taken from days 214, 215, 216

Monitor to monitor correlation

	Channel					
	1	2	3	6(a)	7	8
1	-	.9796	.9425	-	.8550	.8378
2	.9796	-	.9384	-	.9138	.8145
3	.9425	.9384	-	-	.8604	.7050
6(a)	-	-	-	-	-	-
7	.8550	.9138	.8604	-	-	.9014(b)
8	.8378	.8145	.7050	-	.9014(b)	-

Correlation of monitors to Reference method

Channel					
1	2	3	6	7	8
.8281	.2890	.9533	-	-	.1667

(a) unit not operational

(b) 4 data points including 1 zero and 1 span

TABLE H-7

SHORT TERM STABILITY

Time	Level	Channel 1	2	3	6	7	8
		mv					
	zero	0	-	-.23	-.84	3.10	.61
	"	0	-.19	-.22	-.72	3.10	1.56
	"	0	-.10	-.23	-1.40	3.00	1.61
	"	0	-.19	-.22	-1.01	3.10	.41
	"	0	-.13	-.26	-.93	3.10	1.35
	Std. Dev.	0	.809	.016	.258	.045	.559
	646	78.60	2.47	6.12	.81	47.80	1.51
		78.90	2.48	6.11	.46	47.50	1.29
		78.80	2.51	6.11	.67	47.40	.52
		78.30	2.52	6.13	.71	47.60	.68
		78.60	2.56	6.10	.72	48.10	1.31
	Std. Dev.	.23	.036	.011	.13	.277	.434
	859	99.00	3.51	8.03	1.57	54.90	3.92
		99.10	3.50	8.01	1.57	54.80	3.91
		99.00	3.56	8.00	1.62	54.90	2.70
		99.20	3.50	8.02	1.62	55.20	2.74
		89.30	3.57	8.04	1.58	55.30	3.48
	Std. Dev.	.130	.034	.016	.026	.217	.602
	216	25.80	.71	1.42	.41	30.70	.53
		25.90	.81	1.42	.40	30.50	1.65
		26.10	.76	1.43	.45	30.50	1.49
		25.80	.76	1.42	.41	30.40	1.09
		25.80	.77	1.41	.41	30.40	.63
	Std. Dev.	.130	.036	.007	.019	.122	.508
	Average S.D.	.016mv	.035	.0125	.108	.165	.525
			.229				
	Span mv	100	5.0	10.0	2.0	60.0	5
Short term deviations,% span		.16%	.7%	.12%	5.4%	.27%	10.5%

Table H-8

IDENTIFICATION OF MONITORING INSTRUMENTATION

DATA CHANNEL	
1	Calibrated Instruments MSK-SO_2-E_2
2	Dupont Model 460
3	Intertech Model URAS-2
6	Dynasciences Model SS 330
7	ITT Barton Model 400
8	Bendix UNOR-6

TABLE H-9

	PPM	Channel 1	2	3	6	7	8	
	Zero (a)	0	0	-.23	-.98	3.08	1.11	
	646	78.64	2.51	6.35	1.65	44.60	-.05	
	216	25.88	.76	1.65	1.40	27.42	-.02	
span	1036	98.78	4.24	10.01	2.60	48.06	1.49	
	413	49.48	1.64	3.64	2.05	44.70	.88	
	859	99.12	3.53	8.25	2.57	51.94	2.24	
	regression slope	10.00	235.5	97.52	523.66	28.89		ppm/mv
	intercept	-70.2	36.7	50.79	-441.6	-618		ppm
	single point slope	10.48	244.3	103.5	398.5	21.56		ppm/mv

TABLE H-10

PPM Value	Remarks	Channel 1	2	3	6	7	8
646	Single point pred.	824	613.2	657.2	657	961.6	
	Lin. regression pred.	716.2	627.8	670.0	422	670.4	
216	Single point pred.	271.2	185.7	170.8	558	591.2	
	Lin. regress. pred.	188.6	215.7	211.7	291.5	179	
413	Single point pred.	518.6	400.6	376.7	816.9	963.7	
	Lin. regress. pred.	424.6	422.9	405.8	631.9	673	
859	Single point pred.	1039	862.4	853.9	1024.1	1119.8	
	Lin. regress. pred.	921	868.0	855.3	904	882	
	Single point calibration vs "True Value ppm"						
	Error, $\bar{x}$	129	18.0	18.8	230.5	375.6	
	V	2748.5	214.9	522.7	23739.	11859.8	
	SD	52.4	14.7	22.86	154.1	108.9	
	N	4	4	4	4	4	
	$\bar{x}$, % span	13%	1.8%	1.9%	23%	37.6%	
	Linear regression (5 point) calibration vs "true value"						
	Error, $\bar{x}$ ppm	29.1	.17	2.5	28.9	67.5	
	V	1567.5	127.5	156.3	25622	12962	
	SD	39.6	11.29	12.5	160	113.9	
	N	4	4	4	4	4	
	$\bar{x}$, % span	2.9%	.02%	.25%	2.9%	6.7%	

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The conclusions which may be drawn from the data acquired during the program are to be used for several purposes.

The original objective of the program was to provide the Division of Control Systems with the technical information necessary to select instrumentation for in-house and contract SO_2 control technology development programs.

For this immediate need, on the basis of data from the field test program, the following equipment is recommended for use in SO_2 control technology development programs:

a. Calibrated Instruments Co. model MSK-SO_2-E_1 conductometric SO_2 analyzer installed according to schematic 521-51/2.

b. DuPont model 460 ultraviolet SO_2 analyzer when calibration gas standards are used instead of the optical calibration filter for calibration purposes.

c. Intertech model URAS-2 non-dispersive infrared SO_2 analyzer when used with model 7651 probe and filter, model 7865 sample conditioning unit and model CMR 5869 auto zero and calibration units. The CMR 5869 unit shall be set at 8 hour intervals.

These recommendations are made on the basis of:

a. Proven reliability and performance.

b. The availability of the unit as a complete system.

The specifications suggested in appendix B-1 and B-2 were found to be too rigid for the type of field service which is found in this application. Therefore, the judgements as to the performance of these systems were made in a largely subjective manner rather than by comparison with fixed criteria. We do not feel that this approach diminishes the validity of the conclusions, but rather indicates that we aimed our sights at too high a level of performance before obtaining the field experience.

The second objective of this program was to define the state-of-the-art in SO_2 monitoring techniques for the Environmental Protection Agency, in order that EPA could make basic decisions as to the availability of

equipment for possible monitoring requirements; to provide a basis for future Research and Development programs; to provide an information base for providing "guidance on the selection and use of continuous monitoring instrumentation as required by Part 60, Chapter I, Title 40, Code of Federal Regulations."

The conclusions from interpretation of the data in this report concerning the definition of the state-of-the-art in SO_2 monitoring are:

(a) There is equipment available which is adequate for the monitoring purpose required by the New Source Performance Standards of December 23, 1971.

(b) The equipment which does operate properly is that which is available as a complete system consisting of probe, particulate filtration, sample conditioning and analyzer equipment. The Calibrated Instruments and Intertech units listed on the previous page are German built units which have 4 to 6 years of operating experience in stack SO_2 monitoring.

(c) No particular measurement technique is superior to all others. Acceptability depends on a particular implementation of the idea in the analyzer and the supporting sampling equipment. For example, the failure of the Dynasciences unit on channel 3 was probably due to our original insufficient temperature conditioning of the sample and the degradation of the sensing cell under a hot gas stream. If the unit was retested using the sampling systems since developed and made available by the manufacturer, the unit would probably exhibit reasonable performance.

(d) A major operational problem encountered with most of the units was the variance or instability of the "zero" setting (Tables H-5 and H-7). The consistency of the "zero" of the unit on channel one was due to the self-zero or balancing of the unit each measurement cycle. The units on channels 2 and 3 contained

zero correction circuitry which operated on a longer time cycle (30 minutes to 4 hours), and thus, exhibited a larger "zero band" around the automatic set point. Channels 6, 7, and 8 had no automatic zero correction circuitry.

The following are recommendations for future research and development programs to improve stationary source monitoring systems.

(a) Development of improved particulate and H_2O vapor removal devices to be used with existing analyzer equipment.

(b) Development of automatic zero and calibration drift correction devices for use on existing equipment.

(c) Improvement in the zero and calibration stability of existing units.

(d) Development of improved calibration devices and techniques.

(e) Development of extractive sampling monitoring systems which do not require removal of particulate and H_2O vapor or are more tolerant of these substances and do not require complete removal.

(f) Development of in situ monitoring systems which do not require sampling and conditioning systems.

(g) A thorough investigation of the losses and conversions of poilutants in sampling and sample conditioning systems while removing particulate matter and water vapor.

It is further recommended that a periodic re-examination of the state of the art in SO_2 monitoring be performed. A number of new analysis techniques as well as major product improvements have appeared on the commercial market even as this program was underway.

Manufacturers should be encouraged to use analytically verified calibration gases as primary standards rather than electrical offsets or optical absorption filters. The latter are very convenient but have proved less than completely reliable in actual service and do not allow functional checking of the sampling system.

The manufacturers are also encouraged to provide complete "turnkey" installation service with their monitoring systems. The installation difficulties encountered by even the experienced TRW personnel indicates that normal plant operating personnel would have a very difficult time installing and putting into operation most units. This is another reason for treating the monitoring equipment as a complete "system."